

CHEMODYNAMIC BEHAVIOR OF COMPLEX MIXTURES:
LIQUID-LIQUID PARTITIONING AND SORPTION OF
ORGANIC CONTAMINANTS FROM MIXED SOLVENTS

by

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1993

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ACKNOWLEDGEMENTS

I want to thank my committee members Professor Suresh Rao, Dean Rhue, Joe Delfino, Kirk Hatfield and John Zachara for support and helpful guidance leading to the successful completion of this project. I especially want to thank Dr. Rao for his continual contribution to both my personal and professional growth. The exceptional role Dr. Rao has played as my chairman can be best summarized by his most recently awarded title of Graduate Research Professor.

I thank my colleagues Dr. Arthur Hornsby, Ron Jessup, Lynn Wood, Dr. Mark Brusseau, Dr. Ken Van Reese, Dr. Sam Traina, Cheryl Bellin, Denie Augustijn, Dong Ping Dai, Itaru Okuda, and Dr. Peter Nkedi-Kizza for their assistance, support, and friendship. Special thanks go to Cheryl Bellin for her assistance in the acid/base titrations, Itaru Okuda for the UNIFAC simulations, Dr. Mary Collins and Dr. Ron Kuehl for providing numerous subsamples of Webster soil from Iowa, Vicki Neary for her technical assistance in the completion of the laboratory experiments, and Candace Biggerstaff for her help in the preparation and submission of my final draft.

It has been a pleasure to be affiliated with the Soil and Water Science Department at the University of Florida through both employment and education,

and I would like to acknowledge both staff and faculty for their continual support throughout the past fourteen years. I also thank my family, as well as two dear friends, Donna English and Dagne Hartman, whose long-suffering and support have not gone unnoticed, and God for His unfailing grace, love, and guidance. I would also like to acknowledge the unique inspiration I've received from Dr. Jim Davidson and Dr. George Bailey.

The financial support I received from Dr. Rao as my major professor and supervisor, as well as the Subsurface Science Program, United States Department of Energy through a contract (DE-AC06-76RLO) to Battelle PNL; United States Environmental Protection Agency through a cooperative agreement (CR-814512); and the Electric Power Research Institute (contract #RP-2879-7) is gratefully acknowledged.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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August 1993

Chairman: Dr. P.S.C. Rao

Major Department: Soil and Water Science

Contamination of soils and water at waste disposal sites commonly involves various combinations of nonpolar or hydrophobic organic chemicals (HOCs) and hydrophobic ionogenic organic chemicals (HIOCs), as well as mixtures of water and one or more organic cosolvents (either completely or partially miscible in water). Emphasis of this work was on understanding the chemodynamics of such complex mixtures, specifically solubility and sorption. Experimental and theoretical analysis presented has focused on: (1) liquid-liquid partitioning behavior of aromatic hydrocarbons between environmentally relevant organic immiscible liquids (OILs) and water; and (2) the solubility and sorption of HIOCs by soils from completely miscible organic solvent/water mixtures.

Partition coefficients for several HOCs were either measured or compiled from the literature for a wide range of OILs (e.g., gasoline, diesel fuel, motor oil, and coal tar). The use of the UNIFAC (UNIQUAC Functional Group Activity Coefficient) model to estimate the likely nonidealities resulting from interactions between components in these complex OILs is also presented. Both the UNIFAC simulations and the observed OIL-water partition coefficients suggest that nonideality is sufficiently small. Thus, the use of Raoult's law convention for activity coefficients in conjunction with super-cooled liquid solubilities was considered adequate in assessing the partitioning of HOCs between several OILs and water.

The role of solute hydrophobicity and acidity, solvent type, and pH on the sorption of organic acids by a surface soil from mixed solvents was investigated. Predictions of a model that incorporated effects of cosolvent-enhanced solubility and cosolvent-suppressed speciation were compared to measured data. Sorption of neutral benzoic acid was observed to decrease with increasing methanol content, while benzoate sorption increased. Effects of specific solvent and solute properties were investigated by measuring (1) benzoic acid sorption from additional binary mixtures of water and cosolvents with a wide range in solvent properties and (2) sorption of several substituted carboxylic acids from methanol/water solutions. Of the different solute-solvent combinations investigated, enhanced sorption by soils was only observed with carboxylic acids in the presence of methanol or dimethylsulfoxide (DMSO). It was postulated that enhanced sorption resulted from hydrogen-bonding interactions combined with the formation of heterogeneous solvation shells about the solute and the sorbent.

CHAPTER 1 INTRODUCTION

Environmental contamination problems at most industrial waste disposal sites or spill sites commonly involve wastes consisting of complex mixtures of organic and inorganic chemicals. Complex mixtures are defined here as those systems comprising multiple organic solutes and multiple solvents. The solute mixtures of interest might consist of various combinations of nonpolar or hydrophobic organic chemicals (HOCs) and hydrophobic ionogenic organic chemicals (HIOCs). The solvent may be a mixture of water and one or more organic cosolvents (either completely or partially miscible in water). Solvent mixtures of interest may consist of water and cosolvents in a single, homogeneous liquid phase, or multi-phases that form at least two distinct liquid phases. The behavior of such mixtures is not well understood because the primary chemodynamic properties have usually been characterized in aqueous solutions which are simple in composition relative to many waste mixtures found at or near disposal/spill sites. Several researchers have made considerable efforts during the past decade to investigate the primary processes (e.g., solubility, sorption, transport) governing the environmental dynamics of organic chemicals in complex mixtures.

The release and migration of organic constituents from a waste disposal/spill source will produce a contaminant plume, either in the vadose zone or in the saturated zone or both. The contaminant plume composition will vary with time and

distance as the plume size increases. For discussing solubility and sorption processes within the plume, three separate regions may be considered: a *near-field region*, a *transition zone*, and a *far-field region*. The basis for such a distinction is not the distance from the contaminant source. Rather, the criterion employed to designate these regions is the chemistry of the contaminant mixture within the plume as contrasted to the waste.

In the near-field region, corresponding to the source itself and its immediate vicinity, the composition and concentrations of most waste constituents are similar to that in the waste. There are usually two, possibly three, liquid phases in this region. This would be the case, for example in the vadose zone, at waste disposal sites where we may find both "dense" and "light" organic immiscible liquids (OILs) and an aqueous phase as well as a vapor phase. In the transition zone, if it occurs in the saturated zone, the solution phase is likely to be predominantly a single-phase, homogeneous liquid made up of water and varying amounts of cosolvents (if they were present in the near-field region). The concentration of one or more waste constituents may be so high that approximations based on expected behavior in dilute aqueous solutions are often found to be inadequate. Finally, the far-field region corresponds to that region of the plume in which the waste constituents are present in an aqueous solution. Most of these chemicals will be at concentrations well below their aqueous solubility limits. During migration of the contaminant plume through the vadose zone and the saturated zone, chromatographic separation of the waste constituents occurs due to their different mobilities. Furthermore, dilution resulting from hydrodynamic dispersion and attenuation resulting from abiotic/biotic

transformations could decrease contaminant concentrations. Thus, high concentrations of multiple contaminants are less likely to be found as the distance from the source increases. Nevertheless, it is possible that these contaminant concentrations may be higher than the standards set by regulatory agencies.

Partitioning from Multi-phasic Liquids

An understanding of solubility (or partitioning) of HOCs from complex OILs is essential for predicting organic contaminant release from mixtures such as fuels (e.g., gasoline, diesel, kerosene) and industrial wastes (coal tar, creosote). The properties of an organic mixture complex only in composition are determined by the properties of its pure components and their concentrations in the mixture. This implies that the chemicals of interest behave ideally in the matrix containing them. Under these conditions, the concentration in the aqueous phase of a chemical is proportional to the mole fraction of the chemical in the organic phase corresponding to Raoult's law. With the stated assumptions, the concentrations of a chemical in the aqueous phase in contact with a complex mixture can be predicted using the following simplified expression based on Raoult's law:

$$C_w = x_o S_1 \quad (1-1)$$

where C_w is the chemical's concentration (moles/L) in the aqueous phase in equilibrium with the organic phase, S_1 is the aqueous solubility (moles/L) of the pure liquid chemical, and x_o is the mole fraction of the chemical in the organic phase. The derivation of Eq. (1-1) was based on the pure liquid chemical as the standard state.

Many components of interest are solid in their pure form at standard state; however, Eq. (1-1) can be extended to solid solutes by employing hypothetical super-cooled liquid solubilities (S_{act}).

Raoult's law is applicable to a vast number of mixtures of organic chemicals and its use in predicting aqueous phase concentrations in contact with a complex organic mixture is invaluable. These mixtures may be considered complex based on the number of chemicals that constitute the mixture. On the other hand, complexity of a mixture can be defined by considering how the properties of the mixture deviate from some "ideal" behavior, regardless of the number of components. The former view corresponds to a mixture being *complex in composition*, whereas the latter implies *complexity in behavior*. The important point is that a mixture can be complex in composition without being complex in behavior and vice versa.

In general terms, structurally similar chemicals are likely to form "ideal" mixtures, and solubility of such mixtures can then be estimated using Raoult's law. A simple example of the application of Raoult's law is shown in Figure 1-1A for a mixture of two structurally similar compounds, benzene and toluene. The pure aqueous compound solubilities of benzene and toluene are 23.1 and 5.60 mmol/L, respectively. Note that the pure compound solubilities are observed only in the absence of the second component (i.e., only when $x_0 = 0$ or 1). The concentration of either compound in the mixture is attenuated by the presence of the other. The excellent agreement between the measured results and those predicted from Raoult's law (lines) clearly exemplifies the role of mole-fraction on solubility.

In contrast, a mixture of benzene and n-octanol illustrates a system simple in composition, yet nonideal in behavior. Deviations from Raoult's law assuming ideal behavior are evident in Figure 1-1B. Such deviations, however, are not surprising when we consider the dissimilarity in the chemical nature of these two components. Benzene is a hydrophobic aromatic compound while octanol is an alkane with a polar functional group (-OH). The two illustrations given in Figure 1-1 were for compositionally simple mixtures. However, in most environmental scenarios, mixtures with a much larger number of constituents are of interest.

Deviations from ideal behavior can arise if the activity coefficient of the solute in the organic phase is not unity and/or if the solute activity in the aqueous phase is significantly impacted by the presence of other components. A number of computational schemes are available to estimate various activity coefficients such that liquid-liquid partitioning for nonideal mixtures can be evaluated. One of the most frequently used models for this purpose is the UNIFAC (UNIQUE Functional-Group Activity Coefficient) model proposed by Prausnitz et al. 1980). This model is based on the UNIFAC model (Abrams and Prausnitz, 1975) and the solution-of-group concept (Wilson and Deal, 1962). In this model, a mixture of different chemicals is treated as a mixture of functional groups constituting the components in the mixture. The interactions between functional groups in the mixture and the likely nonidealities, resulting from such interactions, are calculated in order to estimate the activity coefficient of a chemical for a specified phase. Calculations based on the UNIFAC model require the values for group interaction parameters as well as the mole fraction of each component in the mixture. The interaction

parameters required in the UNIFAC model have been continuously reviewed and updated since the model was first introduced (Skjold-Jorgensen et al., 1979; Magnussen et al., 1981; Gmehling et al., 1982; Alameida-Macedo et al., 1983; Hansen et al., 1991).

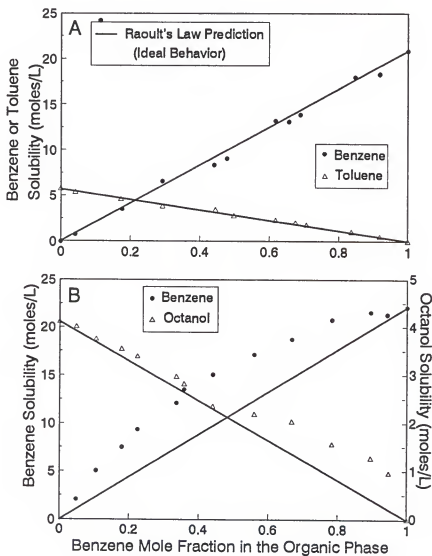


Figure 1-1. Comparison of measured and calculated (Raoult's law) aqueous solubilities in binary mixtures of benzene-toluene (A), and benzene-octanol (B). Data from Sanemesa et al. (1987).

Sorption from Aqueous Solutions

Most of the available data and theories for predicting sorption and transport of organic chemicals may be successfully applied to predict contaminant behavior in the far-field region (i.e., dilute aqueous solutions). The following section will highlight the information available on equilibrium sorption of organic chemicals relevant to this dissertation work.

Sorption is one of the dominant processes affecting the mobility of organic contaminants in soils and groundwater. This process can be conceptualized either as binding at a two-dimensional interface of the sorbent or as a partitioning into the three-dimensional bulk of the sorbent. Several methods for estimating the magnitude of sorption for organic contaminants have been developed based on the chemical and physical properties of the sorbate, the sorbent, and the solvent.

Hydrophobic Organic Compounds (HOCs)

Equilibrium sorption of hydrophobic organic compounds (HOCs) by soils and sediments has been successfully predicted in many cases by the "solvophobic theory" and the use of linear free energy relationships (LFER). Excellent log-log, linear relationships have been reported between K_{oc} , the sorption coefficient normalized to the fraction of organic carbon (OC) of the sorbent, and K_{ow} , the octanol-water partition coefficient for several HOCs (c.f., Dzombak and Luthy, 1984; Karickhoff, 1981; 1984; Kenega and Goring, 1980). Linear relationships have also been found between $\log K_{oc}$ and solute hydrophobic surface area (HSA) (Dzombak and Luthy, 1984; Rao et al., 1985) and solute molecular connectivity (Sabljic, 1984; 1987). The

different slopes and intercepts found in these regression equations are predominantly determined by the characteristics of a group of compounds (i.e., class, degree of hydrophobicity, and structure), while the sorbent properties other than OC appear to have only minor impact in most cases (Karickhoff, 1981, 1984; Schwarzenbach and Westall, 1985). The equations derived from LFER and experimental data obtained for only a few sorbents provide reasonable predictions of HOC distribution in diverse soil-water and sediment-water systems. However, the limitations of the K_{oc} concept have been pointed out by a number of authors (e.g., Mingelgrin and Gerstl, 1983; Green and Karickhoff, 1991; Gerstl, 1990). The two main concerns involve the contribution of adsorption on mineral constituents and the possibility of site-specific interactions between functional moieties of the solute and the sorbent.

Hydrophobic ionogenic organic compounds (HIOCs)

For hydrophobic, ionogenic organic compounds (HIOCs), several factors (e.g., speciation, soil-solution pH, sorbent-surface pH, charge, ionic strength, ionic composition, multiple solutes) make predicting sorption from a single parameter difficult due to additional mechanisms that must be considered. Several mechanisms proposed in the literature for sorption of organic solutes from aqueous solutions include: hydrophobic interactions; London-van der Waals or dispersion forces; hydrogen bonding; cation and water bridging; cation and anion exchange; ligand exchange; protonation; covalent bonding or chemisorption; and interlayer adsorption (Koskinen and Harper, 1990). Hydrophobic interactions are driven by weak solute-solvent interactions and the preference of an organic molecule to be near an organic

surface; thus, strong inverse correlations are observed between K_{oc} and solubility of HOCs. London-van der Waals forces result from correlations in the electron movement between molecules that produce a small net electrostatic attraction. Although small in magnitude (2-4 kJ/mol), these interactions are additive and have been found to be significant for the sorption of large neutral polymeric solutes.

Hydrogen bonding interactions involve the electrostatic interaction between protons and electronegative atoms, and can be stronger than dispersion forces (2-60 kJ/mol) (Kohl and Taylor, 1961; Stumm et al., 1980). Hydrogen-bonding interactions may occur with both inorganic and organic surfaces, but for soils interactions with organic matter are more important due to the abundance of carbonyl-type functional groups (Sposito, 1984).

Cation bridging results if a polar organic functional group displaces a water molecule from the primary hydration shell of an exchangeable cation (i.e., formation of an inner-sphere complex), whereas water bridging results when interaction occurs without displacement of the hydrating water molecules (i.e., outer-sphere complexation) (Farmer and Russell, 1967). The occurrence of cation bridging versus water bridging will be a function of the heat of cation hydration, which varies with cation size and charge (i.e., charge density). For example, water bridging would be preferred in a Ca^{+2} -saturated sorbent due to its large negative heat of hydration ($\Delta H = -377$ kcal/mol) compared to a saturation with K^+ ($\Delta H = -75$ kcal/mol) (Bailey et al., 1968).

Ion exchange involves the exchange of a cation or an anion for another ion of similar charge at specific binding sites. Cation exchange is of much greater

importance for most soils due to the predominance of negatively charged surfaces. Similar to cation bridging, but a much stronger interaction, is ligand exchange which involves the formation of an inner-sphere complex with a structural cation of a soil mineral (i.e., displacement of either water or hydroxyl molecules from iron or aluminum oxides)(Stumm et al., 1980; Kummert and Stumm, 1980). Ligand exchange is commonly believed to be the mechanism responsible for the adsorption of oxyanions. Likewise, protonation involves the formation of charge-transfer complexes with protons on mineral surfaces and organic functional groups such as amino and carbonyl groups. Interlayer adsorption involves the sorption and entrapment of solute molecules within clay interlayers. From infrared spectroscopic data, Farmer and Russell (1967) infer that benzoic acid enters the interlayer space as an unionized monomer, and then the oxygens from both the hydroxyl and carbonyl groups become coordinated to the interlayer cation.

In many cases, it is difficult to definitively conclude what particular mechanism is responsible for the observed sorption; however, frequently we can predict the magnitude of sorption by incorporation a few parameters. For example, on the basis of an analysis of a large data set for pentachlorophenol (PCP) sorption from aqueous solutions by several sorbents over a broad pH range, Lee et al. (1990) showed that equilibrium sorption could be predicted with a knowledge of pH, organic carbon (OC) content of the soil, and the acid dissociation constant (pK_a) for PCP. Their model for predicting sorption coefficient is:

$$K_{oc} = K_{oc,n} \phi_n + K_{oc,i} (1 - \phi_n) \quad (1-2)$$

where

$$\phi_n = (1 + 10^{pH-pK_a})^{-1} \quad (1-3)$$

and K is the measured distribution ratio for the sorbed- and solution-phase concentrations; $K_{oc} = (K/OC)$; OC is the soil organic carbon content (mass fraction); ϕ_n is the fraction of the neutral HIOC; and the subscripts n and i refer to neutral and ionized species, respectively.

Sorption data compiled from the literature for several other organic acids could be, in most cases, adequately described by Eq. (1-2). Shown in Figure 1-2 for example, is reasonable predictions by Eq. (1-2) of OC normalized sorption of the herbicide flumetsulam compiled from Fontaine et al. (1991) for several soils.

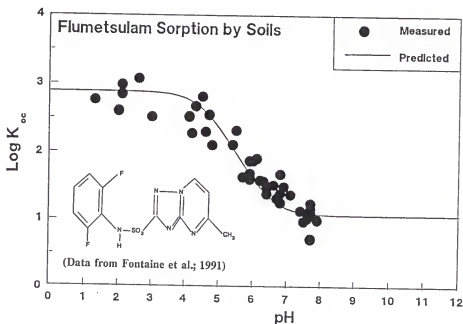


Figure 1-2. Measured and predicted sorption of flumetsulam by several soils normalized to organic carbon content plotted as a function of pH. (Data from Fontaine et al., 1991)

Data compiled from Kukowski (1989) and Jafvert (1990) for sorption of a variety of organic acids by soils from aqueous solutions are shown in Figure 1-3. To facilitate viewing of sorption data from different solute-sorbent combinations simultaneously, the pH scale is referenced to the solute's pK_a (i.e., $pH - pK_a$) and sorption is scaled to the solute's K_n and K_i values as follows: $(K_{obs} - K_i)/(K_n - K_i)$. Values for K_n and K_i were estimated in the sorption experiments where $pH - pK_a$ was less than or greater than one (i.e., acid was predominately neutral or ionic, respectively). Agreement of Eq. (1-2) with the measured data suggests that the measured bulk soil-solution pH is representative of the pH seen by the solute, and that K_n and K_i are additive. Note that this does not infer a particular sorption mechanism or that the mechanisms for the neutral and ionized species are the same.

For organic bases, sorption is affected by similar factors as for organic acids. However, ion-exchange has been shown to be the controlling sorption mechanism for organic bases even at pH values as much as two units greater than the solute pK_a (Zachara et al., 1987, 1990; Ainsworth et al., 1987; Bellin, 1993). Competitive sorption between compounds has also been observed for organic cations (Zachara et al., 1987; Felice et al., 1985). In contrast, for HOCs and neutral HIOCs competition is minimal (Zachara et al., 1987; Karickhoff et al., 1979; Schwarzenbach and Westall, 1981; Chiou et al., 1983; MacIntyre and deFur, 1985; Rao et al., 1986). The predominance of ion-exchange in the sorption of organic bases suggests the use of a sorption coefficient normalized to the cation exchange capacity of the sorbent as a first approximation, analogous to the use of K_{oc} for describing sorption of HOCs.

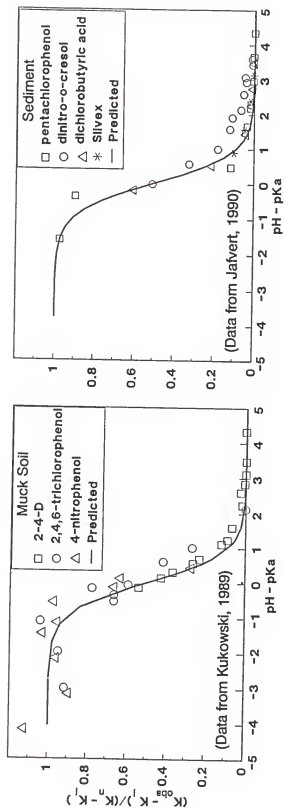


Figure 1-3. Normalized sorption coefficients for several organic acids plotted as a function of $pH - pK_a$. [Data from Kukowski (1989) and Jafvert (1990)]

Cosolvency

The effects on solubility and sorption (hence, on transport) of organic chemicals upon addition of one or more organic cosolvents to an aqueous solution are defined here as *cosolvency*. This section will focus on the most significant interactions affecting solubility and sorption of both HOCs and HIOCS. Such interactions include solute-cosolvent, cosolvent-cosolvent, and cosolvent-water interactions for solubility; for sorption, solvent-sorbent interactions must also be considered.

Solubility in Mixed Solvents

The log-linear cosolvency model and the UNIFAC model are among the theoretical approaches that have been used to examine cosolvent effects on solubility (Fu and Luthy, 1986a; Pinal et al., 1990). The log-linear cosolvency model (Yalkowsky and Roseman, 1981) is based on the central assumption that the logarithm of the solute solubility in a mixed solvent is given by the weighted-average of the logarithms of solubilities in the component solvents in the mixture; the weighting coefficient is taken to be the volume fraction of each solvent component. Thus,

$$\log S_m = \sum f_i \log S_i \quad (1-4)$$

where S is solubility (mg/L), f is volume fraction of the solvent, and the subscript m denotes mixed solvent and i the i -th cosolvent. Note that averaging the logarithms of solubilities is equivalent to averaging the free energies of solution in different solvents in the mixture.

In many cases the UNIFAC model may be preferred over the log-linear model because (i) it has a more sound theoretical basis, (ii) activity coefficients in mixtures can be calculated given only pure component data, and (iii) all possible interactions among the components in the mixture are explicitly considered. A limitation of the UNIFAC model, however, is that although the group interaction parameters required to estimate the solute activity coefficients are continuously reviewed and updated, their values are not available for a number of systems of interest here. Also, there are both experimentally-based (Banerjee, 1985; Arbuckle, 1986) and theoretically based (Pinal, 1988) reasons that limit the applicability of UNIFAC to aqueous systems.

A convenient measure of the impact of a cosolvent on the solubility of an organic chemical is the *cosolvency power* (σ), which is defined as

$$\sigma = \log \frac{S_c}{S_w} \quad (1-5)$$

where the subscripts c and w refer to neat cosolvent and pure water, respectively. HOC solubility in organic solvents is larger than that in water, thus $\sigma > 0$. Larger values of σ indicate a greater solubilizing power of the solvent for a specific solute.

Rubino and Yalkowsky (1987a) and Pinal et al. (1990) have shown that σ values can be viewed as being equivalent to hypothetical partition coefficients for the HOC between a cosolvent and water. Morris et al. (1988) have shown that σ values can be correlated to HOC octanol-water partition coefficient (K_{ow}) as follows:

$$\sigma = a \log K_{ow} + b \quad (1-6)$$

where a and b are empirical constants unique for a given cosolvent. Other cosolvent and solute properties may also be used to estimate σ values (Rubino and Yalkowsky, 1987a,b; Morris et al., 1988).

Although both Eq. (1-5) and (1-6) provide useful first-order approximations of the cosolvency power of a solvent for a solute, measured HOC solubility profiles in solvent mixtures often exhibit deviations from the expected log-linear behavior primarily due to solvent-cosolvent interactions. The observed cosolvency in a binary mixed solvent can be more generally defined as,

$$\log S_b = \log S_w + \sigma_c f_c \quad (1-7)$$

where S_b is the solubility in the binary mixture.

Equilibrium Sorption from Mixed Solvents

Hydrophobic Organic Chemicals (HOCs)

A log-linear cosolvency model describing the decrease in sorption of HOCs with increasing f_c in a binary solvent is given by (Rao et al., 1985; Fu and Luthy, 1986b):

$$\log K_b = \log K_w - \alpha \sigma_c f_c \quad (1-8)$$

where K is the equilibrium sorption coefficient (mL/g), α is an empirical constant for describing solvent-sorbent interactions, and the subscript b stands for binary mixed solvent.

An extensive amount of data has shown that in binary mixed solvents, HOC solubility increases and sorption decreases in a log-linear manner as the volume fraction of the organic cosolvent increases (Rao et al., 1985, 1986, 1989, 1990; Nkedi-Kizza et al., 1985, 1987, 1989; Woodburn et al., 1986; Fu and Luthy, 1986a,b; Yalkowsky 1985, 1987; Rubino and Yalkowsky, 1985, 1987a,b,c; Walters and Guiseppi-Ellie, 1988). These experimental findings are consistent with the predictions of both the UNIFAC model and the log-linear cosolvency model. Also, for the sorption of HOCs, solvent-solute interactions as described by solubility are found to predominate such that the impact of solvent-sorbent interactions has been considered minor. However, for solutes containing specific functional groups, the impact of the cosolvent on the sorbent may have considerable impact.

Hydrophobic Ionizable Organic Chemicals (HIOCs)

For hydrophobic ionogenic compounds (HIOCs) of environmental interest, data on solubility, sorption, and transport in mixed solvents are limited. However, pharmaceutical literature contains solubility data for several drugs spanning a wide polarity range. Yalkowsky and Roseman (1981) observed that as solute polarity increases relative to the solvent, the solubilization curves become increasingly more parabolic in shape until an inverse relationship occurs (i.e., decreased solubility with cosolvent additions). Such behavior is explained on the basis of the solute-solute and solute-cosolvent interactions.

The sorption of HIOCs from mixed solvents has received little research attention to date. For several HIOCs of environmental relevance ($\log K_{ow} > 1.0$),

solubility does increase with increasing f_c ; thus, a decrease in sorption is expected. Fu and Luthy (1986b) observed an inverse log-linear behavior in the sorption by three different soils of naphthol, quinoline, and dichloroaniline in methanol/water and acetone/water solutions up to 50% by volume. Similar behavior was observed by Zachara et al. (1986) for quinoline sorption by a natural clay isolate and montmorillonite in the same binary mixtures. However, for the sorption of an ionizable fluorescent dye (Rhodamine WT) from binary mixtures of methanol/water and acetone/water, Soerens and Sabatini (1992) observed adherence to the log-linear model only for cosolvent fractions less than 30%, while at higher fractions sorption increased.

For hydrophobic, ionogenic organic compounds (HIOCs), several factors (e.g., speciation, soil-solution pH, sorbent-surface pH, charge, ionic strength, ionic composition, multiple solutes) make predicting sorption from a single parameter difficult due to additional mechanisms that must be considered. As discussed previously, prediction of HIOC sorption by soils from aqueous solutions is already complicated due to the potential for a variety of different sorption mechanisms. Prediction of HIOC sorption from mixed solvents is further confounded by a number of indirect effects resulting from cosolvent-induced phenomena occurring either in the solution phase or on the sorbent. For example, for an organic acid in solvents of low dielectric constants (e.g., methanol, acetone, dimethylsulfoxide) an alkaline shift in the solute pK_a results in an increase in the fraction of neutral species. Similar impacts on the ionization of sorbent functional groups and subsequent solute-sorbent interactions must also be considered. Also, the impact of cosolvent-water interactions that have been considered negligible in predicting the chemodynamic behavior of HOCs may become important when assessing the behavior of HIOCs.

In addition, the different propensities of the cosolvent and water to solvate both the solute and the sorbent will be important in understanding the sorption of HIOCs. The existence of codisposal sites, implementation of cosolvents in remediation schemes, and the development of alcohol-based fuels further warrants a better understanding of the behavior of HIOCs in complex solvent mixtures.

Emphasis of this work was on understanding the solubility and sorption of HOCs in multi-phasic mixtures, and of HIOCs in complex miscible-solvent/water mixtures. The liquid-liquid partitioning behavior of aromatic hydrocarbons between environmentally relevant organic immiscible liquids (OILs) and water was investigated. The applicability of Raoult's law was assessed by measuring and compiling partitioning data from several multi-component OILs, and the UNIFAC model was utilized to estimate the likely nonidealities resulting from interactions between components in these complex OILs. These results are discussed in Chapter 2. For the partitioning of HIOCs from binary miscible-cosolvent/water mixtures, the role of solute hydrophobicity and acidity, solvent type, and pH on the sorption of organic acids by a surface soil from mixed solvents was investigated. These studies included (1) sorption of several organic acids from methanol/water solutions (Chapter 3), (2) sorption of benzoic acid and PCP as a function of pH at several fixed methanol/water compositions (Chapter 4), and (3) benzoic acid sorption from additional binary mixtures of water and cosolvents with a wide range in solvent properties, as well as, sorption of several substituted carboxylic acids from methanol/water solutions (Chapter 5). The observed sorption of these HIOCs was assessed in terms of cosolvent-enhanced solubility, cosolvent-induced speciation, as well as specific and nonspecific solvent association mechanisms.

CHAPTER 2

EQUILIBRIUM PARTITIONING OF POLYAROMATIC HYDROCARBONS FROM ORGANIC IMMISCIBLE LIQUIDS INTO WATER

Introduction

Background

Environmental contamination problems at most industrial waste disposal sites or spill sites commonly involve the presence of an immiscible organic phase constituting a multi-phasic waste with multiple components. Of great concern is the transport of organic constituents from these wastes resulting in contamination of soil and water. Near the source of contamination where a separate organic phase is present, solubility is the primary process controlling the release of organic chemicals to the aqueous phase. Therefore, an understanding of the solubility (or partitioning) of polyaromatic hydrocarbons (PAHs) from a complex liquid such as those suggested is essential in predicting contaminant release.

Over the last few years efforts have been made to measure the partitioning of PAHs from environmentally relevant organic liquid wastes such as gasoline, motor oil, diesel fuel, and coal tar. Coal tars are among the most complex organic liquid wastes and comprise a large number of hydrocarbons spanning a broad spectrum of molecular weights. The concentrations of individual constituents in coal tars vary significantly from one manufacturing gas plant (MGP) site to another. The

manufacturing of gas from coal and oil for residential, commercial, and industrial use in the late 1800s and early 1900s resulted in the production of large amounts of coal tar wastes. Eng and Menzies (1985) reported that more than 11 billion gallons of coal tar were generated in the U.S. during the period 1816-1947, but the disposition of several billion gallons is unknown and remains unaccounted. In many cases, the wastes were left on-site in pits or containers, placed in near by ponds or lagoons, or taken to off-site areas for land disposal. Such practices resulted in contamination of soils and groundwater at most former MGP sites. Hydrophobic organic chemicals (HOCs) have been detected at former MGP sites, and are of particular concern due to their potential carcinogenic nature (Guerin, 1978). Several of these compounds have already been included on the U.S. EPA list of priority pollutants.

In the past, it has often been assumed that concentrations of organic contaminant in the aqueous phase leaving a coal tar source would be equal to their corresponding pure-compound aqueous solubilities. This may be a reasonable estimate if the source of interest was composed of a single contaminant (e.g., trichloroethylene, tetrachloroethylene). However, most complex wastes (e.g., coal tar, diesel, gasoline) consist of mixtures of contaminants. These mixtures may be considered complex based on the number of chemicals that constitute the mixture. On the other hand, complexity of a mixture can be defined by considering how the properties of the mixture deviate from some "ideal" behavior, regardless of the number of components. The former view corresponds to a mixture being *complex in composition*, whereas the latter implies *complexity in behavior*. The important

point is that a mixture can be complex in composition without being complex in behavior and vice versa.

To assess the extent of groundwater contamination and the long-term environmental impacts from land disposal or spill sites containing multi-phasic wastes, it is necessary to characterize the total amounts released and the release rates of HOCs from the waste matrix. The properties of an organic mixture complex only in composition are determined by the properties of its pure components and their concentrations in the mixture. This implies that the chemicals of interest behave ideally in the matrix containing them. Under these conditions Raoult's law would suggest that the concentration in the aqueous phase of a chemical is proportional to the mole fraction of the chemical in the organic phase.

This chapter will focus on the use of equilibrium theory to characterize the total amounts of PAHs released from organic liquid wastes. Coal-tar/water partition coefficients for several PAHs were measured from several coal tars spanning a wide range in physical and chemical properties. To estimate aqueous-phase concentrations of PAHs in equilibrium with coal tar, the utility of applying Raoult's law convention for activity coefficients in conjunction with supercooled liquid solubilities for PAHs that are crystalline in their pure form will be assessed. Although the majority of this chapter is on coal tar wastes, a reassessment of diesel fuel/water and gasoline/water partitioning data will also be presented including the use of the UNIFAC (UNQUAC functional group activity coefficient) model to estimate the likely nonidealities resulting from interactions between components in these complex organic liquids.

Theory

The release of a chemical from an organic liquid phase can be estimated from a liquid-liquid partition coefficient (K_d) which is defined as

$$K_d = \frac{C_o}{C_w} \quad (2-1)$$

where C_o and C_w are the molar concentrations (mol/L) of the chemical of interest in the organic and aqueous phases at equilibrium, respectively. The partition coefficients (K) for coal tar, diesel fuel, and gasoline will be designated using subscripts tw , dw , and gw , respectively.

For liquid-liquid partitioning, thermodynamic equilibrium is defined by the equality of the chemical potentials in the aqueous and organic phases. This equality, in conjunction with the choice of pure (liquid) solute as the standard state and the Raoult's law convention for activity coefficients, results in the following expression at equilibrium

$$x_o \gamma_o^* = x_w \gamma_w^* \quad (2-2)$$

where subscripts o and w denote organic and aqueous phases, respectively; x_o and x_w are the respective mole fractions of the chemical in the organic and aqueous phase; γ_o^* is the activity coefficient of the chemical in the organic phase in equilibrium with the aqueous phase; and γ_w^* is the activity coefficient of the chemical in the aqueous phase in equilibrium with the organic phase.

From Eq. (2-2), molar concentration of a solute in the aqueous phase (C_w) can be approximated with the following assumptions: (1) the presence of other

components in the aqueous phase is ignored, i.e., γ_w^* is set equal to the aqueous phase activity coefficient of the solute in equilibrium with the pure solute (γ_w); (2) the solute behaves ideally in the organic phase, i.e., γ_o^* is unity; (3) the aqueous mole fraction solubility ($S_{x,w}$) of the pure liquid solute is equal to $1/\gamma_w$; and (4) the solution is sufficiently dilute (i.e., moles of the solute are small relative to the total moles of solvent; $C = x/\bar{V}$ and $S_l/\bar{V}_w = S_{x,w}$ where S_l is the aqueous solubility of the pure liquid solute in moles/L) and \bar{V}_w is the molar volume of water. Application of these four assumptions yields

$$C_w = x_o S_l \quad (2-3)$$

Therefore, the partition coefficient (Eq. 2-1) for a solute can be approximated as follows,

$$K_d = \frac{C_o}{x_o S_l} \quad (2-3)$$

For mixtures comprising a large number of constituents, each contributing a small fraction to the total, x_o/C_o can be replaced by the molar volume (\bar{V}_o , L/mole) of the organic phase. The molar volume can then be approximated by the ratio of the average molecular weight (MW_o , g/mole) and density (ρ_o , g/L). The resulting expression for K_d is:

$$K_d = \frac{1}{\bar{V}_o S_l} = \frac{(\rho_o / MW_o)}{S_l} \quad (2-5)$$

Taking logarithms of both sides of Eq. (2-5), it is evident that the inverse relationship between $\log K_d$ and $\log S_l$ results in a unit negative slope and an intercept that is dependent upon the molar volume of the organic phase (i.e., MW_o/ρ_o):

$$\log K_d = -\log S_l - \log \left(\frac{MW_o}{\rho_o} \right) \quad (2-6)$$

Derivation of Eq. (2-6) was based on a choice of the pure liquid solute as the standard state. Most of the PAHs investigated in this study are solids in their pure form; therefore, the hypothetical supercooled liquid solubilities of the solid solutes must be employed. The supercooled liquid solubility (S_l) of a solute at a given temperature can be calculated directly from the solute's measured heat of fusion (ΔH_f) and melting point (T_m) (Yalkowsky, 1980), or alternately can be estimated by assuming a constant entropy of fusion ($\Delta S_f = \Delta H_f/T_m$) for the PAHs of interest (Yalkowsky, 1979; Martin et al., 1979) (see Appendix A).

Application of Raoult's Law for Gasoline, Motor Oil, and Diesel Fuel

The utility of the relationship defined by Eq. (2-6) was successfully demonstrated for several gasolines by Cline et al. (Cline et al., 1991) for several monocyclic aromatic hydrocarbons (MAHs). Gasoline is composed of several branched-chain paraffins, cycloparaffins, alkanes, aromatic compounds, and small amounts of various additives. Results presented by Cline et al. (1991) revealed that although gasoline is complex in composition, MAH partitioning into water behavior was essentially ideal. None of these MAHs exhibit crystalline structure in their pure form which is common to most PAHs. Chen (1993) investigated the applicability of

Raoult's law for the partitioning of MAHs as well as some PAHs from new and used motor oil. Given the absence of experimental artifacts, nonideality was noted for the partitioning of MAHs from the new motor oils, whereas, the one PAH investigated (phenanthrene) partitioning was successfully predicted using Raoult's law and supercooled liquid solubilities. However, Raoult's law appeared applicable within a factor-of-four for the partitioning of both MAHs and several PAHs from used motor oil.

Hagwall (1992) measured the partitioning of several PAHs from diesel fuel into water and concluded that the use of supercooled liquid solubilities (S_{scf}) in applying Raoult's law was not successful. However, Hagwall (1992) used an inaccurate estimation of S_{scf} resulting in a wrong conclusion regarding the applicability of Raoult's law. Using the crystal solubilities (S_w) given in Table 2-1 and assuming a constant ΔS_f of 13.5 eu, a much better relationship was observed between $\log K_{dw}$ and $\log S_l$. In Figure 2-1, the measured $\log K_{dw}$ values are plotted against their $\log S_l$ for the eight PAHs investigated along with the ideal line (solid line) calculated from Eq. (2-6) for each diesel fuel using the MW_o and ρ_o given by Hagwall (1992). For most PAHs in all four diesel fuels, the $\log K_{dw}$ values lie near the ideal line suggesting that the assumption of ideal behavior may be adequate for describing the partitioning of PAHs from diesel fuels to water. The confidence intervals (bars) shown in Figure 2-1 were estimated using an error propagation method (Shoemaker et al., 1980) which incorporates the errors incurred in the analysis of both the neat fuel and aqueous phase concentrations. Arrowheads reflect

the few cases where the propagated error was larger than the average K_{dw} value as was the case for anthracene and fluoranthene. Note that both compounds were present in small quantities in the neat fuel and or analytical problems were encountered in detecting small aqueous phase concentrations. Several factors other than nonideal behavior could result in apparent deviations such as analytical uncertainty in K_{dw} , as well as, errors incurred in the estimations of S_i (i.e., reported S_w values and the use of a constant ΔS_f value).

The success in applying Raoult's law for gasolines, diesel fuels, and motor oils leads to the question of whether ideal behavior can also be assumed for coal tars. Compared to gasolines, diesel fuels, and motor oils coal tars are even more complex in composition, especially because over 60% of their constituents are not known. Gasolines, diesel fuels, and coal tars collected from different sites vary greatly in their composition, but only a small variance exists in their molecular weights (Cline et al., 1991; Hagwall, 1992). In contrast, different coal tars exhibit a wide range in composition, MW_o and ρ_o (EPRI, 1993). The applicability of Raoult's law to tar/water partitioning will be assessed as well as the potential for nonideal behavior.

Table 2-1. Selected physico-chemical properties for the PAHs investigated.

Compound	Melting ^a Point (C°)	Molecular Weight ^a (g/mole)	S _w ^b (mg/L)	log S _l ^d
Naphthalene	80.2	128.2	32	-3.05
1-methylnaphthalene	-22	142.2	27 ^a	-3.72 ^e
2-methylnaphthalene	34	142.2	26 ^c	-3.62
Acenaphthylene	82	152.2	3.93	-4.02
Acenaphthene	93	154.2	3.42	-3.98
Fluorene	116.5	166.2	1.9	-4.03
Phenanthrene	100	178.2	1.0	-4.5
Anthracene	216.3	178.2	0.07	-4.49
Fluoranthene	107	202	0.27	-5.19
Pyrene	150	202	0.16	-4.85
Chrysene	254	228.2	0.006	-5.29
Benzo(a)anthracene	156	228.2	0.0057	-6.29
Benzo(a)pyrene	179	252	0.0038	-6.28

^a Verschuren (1983); ^b Crystal solubility at 25°C (Little, 1981) unless stated otherwise;

^c Miller et al. (1985); ^d Supercooled liquid solubility (moles/L) calculated assuming a constant ΔS_f for PAHs; ^e liquid solute at standard state.

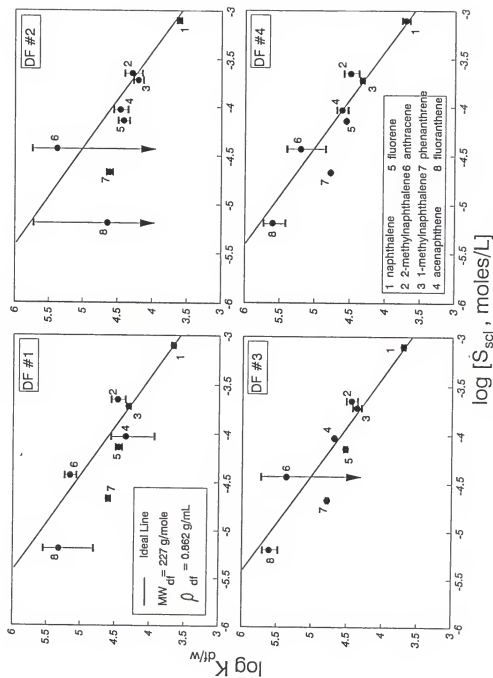


Figure 2-1. $\log K_{aw}$ values plotted versus $\log S_i$ for eight PAHs along with the ideal line (solid line) calculated from Eq. 2-6 for each diesel fuel.

Materials and Methods

Chemicals

For all the PAHs investigated (see Table 2-1) standards were purchased from Aldrich Chemical Co. at >98% purity except for acenaphthene, which was available only at 85% purity. Methylene chloride, the solvent used for the aqueous phase extractions, was purchased from Fisher Scientific at Fisher grade Optima.

Batch Equilibration Technique

Approximately 0.3-0.5 g of coal tar were added to a glass centrifuge tube (nominal volume 40 mL); enough electrolyte solution (0.01 N CaCl_2) was added such that no headspace remained; and tubes were closed with phenolic caps fitted with Teflon-lined septa. Prior to sampling the coal tar for equilibration with an aqueous phase, coal tars were rotated end-over-end at room temperature ($23 \pm 2^\circ\text{C}$) for 12-18 hours. The coal tar/water (0.01 N CaCl_2) mixtures were then equilibrated for 3-7 days in the dark. Preliminary studies where samples were equilibrated for 1, 3, 5, and 7 days showed no measurable differences in PAH concentrations after 3 days. Following centrifugation (300 RCF for 30 minutes) of the equilibrated coal tar/water mixtures, a portion of the aqueous phase (≈ 25 mL) was quantitatively removed for extraction with methylene chloride and subsequent concentration prior to analysis. Due to the large masses of the compounds of interest present in the coal tar phase, experimental artifacts from PAH sorption to the equilibration vessels were considered negligible. To avoid volatilization losses and contamination of the aqueous phase aliquot with the coal tar phase, the aqueous aliquot was removed through the septa using a 50-mL Teflon-backed gas/liquid syringe equipped with a

3-inch needle. The equilibration vessel was vented during sampling by piercing the septa with a second needle.

Following aqueous phase transfers, as much residual water as possible was removed from the equilibration vessel without loss of the coal tar. The coal tar in the equilibration vessel and the cap were rinsed with methylene chloride into a 100-mL volumetric flask and brought to volume. Dissolved coal tar samples were filtered (0.45 μm) prior to analysis. For the coal tar samples from which it was difficult to remove residual water without loss (i.e., thin liquid coal tars), an aliquot of the neat coal tar was sampled for analysis as well.

Chromatographic Analysis

PAH concentrations in the coal tar and aqueous phases were determined using a gas chromatograph (GC) equipped with an ion trap detector (ITD). The GC/ITD method included an HP Ultra 2 column (95% methyl, 5% phenyl polysiloxane, 0.5 micron thickness; 30 cm x 0.32 mm ID); helium as a carrier gas at a flow rate of approximately 1.0 mL/min; temperature gradient program, and an ion trap detector. The temperature gradient program consisted of a 1 minute hold at 50°C; a ramp to 130°C at 30°C/min followed by a 3 minute hold; a ramp to 180°C at 12°C/min followed by a 1 minute hold; a ramp to 240°C at 7°C/min; and a ramp to 300°C at 12°C/min followed by a 15 minute hold. The ITD was set at an electron energy of 70 eV and scanned from 45 to 450 amu at 2 scans/sec. The electron multiplier voltage was 1650 volts and the transfer temperature from the GC was 280°C. Prior to GC analysis, samples were usually spiked with an internal standard consisting of naphthalene- d_8 and anthracene- d_9 .

Results and Discussion

Coal Tar Composition

The coal tars used in this study were received from META Environmental, Inc. Various physical and chemical properties of these coal tars had been characterized (EPRI, 1993), including density, viscosity, water and ash content, average molecular weight, elemental and organic analysis. The ranges observed for these properties in terms of percentages or concentrations are summarized in Table 2-2.

The viscosity of the coal tars ranged from approximately 34 cps to 6600 cps (40°C), with the coal tar consistency varying from thin liquids (ID# 1,4, and 5) to thick liquids (ID# 7) and from soft (ID# 3 and 9) to sticky (ID# 2) "taffy-like" materials. Coal tar viscosity will generally increase with aging and decrease with temperature. Some coal tars had high ash contents, suggesting the presence of other solids. For example, coal tar ID# 7N had a high content (37%) of what appeared to be sand and silt. The PAH concentrations for this coal tar were corrected to represent the mass of PAH present per actual mass of coal tar. For the remaining coal tars an occasional rock or pellet was found, which was easily removed prior to experimentation.

Water content of the thin liquid coal tars was small (<1% mass basis). For the more viscous coal tars, reported water contents were as high as 30% (mass basis); however, high molecular weights and densities for these coal tars strongly suggests that these high water contents were in actuality a sampling artifact. It appears that water may have been trapped as a separate liquid phase within the taffy-like matrix of the coal tar.

Table 2-2. Range of properties observed for eight coal tars (EPRI, 1993).

<u>Physical Properties:</u>	<u>Range</u>	<u>Elemental Analysis:</u>	<u>Range(%)</u>
Ash	0-50%	Carbon	43-90
Water Content	0-30%	Hydrogen	2-7
TOC ^a	40-90%	Nitrogen	<0.5-1
Viscosity ^b	34-6,600 cps (40°C)	Oxygen	1-33%
Density ^c	1.06-1.43 g/mL (24°C)	Sulfur	0.4-4%
MW ^d	230-780 ^e g/mole	Cyanide	<1-580 mg/kg ^h <1-150 mg/kg ⁱ
<u>Organic Compounds</u>	<u>Range (mg/kg)</u>	<u>Metals Analysis</u>	<u>Range (mg/kg)</u>
monocyclics	13-25,300	Arsenic	3-23
polycyclic:		Beryllium	<1
2 & 3 rings	6,800-218,000	Cadmium	<1-4
> 3 rings	12,000-110,000	Lead	1-930
NPAHs ^f	70-1,000	Nickel	2-74
SPAHS ^g	0-4,000	Selenium	<1-5
Pitch		Vanadium	6-230
		Chromium	<1-230

^a Total Organic Carbon; ^b Test Methods ASTM D445 and D88; ^c Test Methods ASTM D70, D369, or D1429; ^d Average molecular weight determined using vapor pressure osmometry; ^e Exception: asphaltene-like tar 1600 g/mole; ^f Nitrogen polyaromatic hydrocarbons; ^g Sulfur polyaromatic hydrocarbons; ^h Determined using EPA Method 4500; ⁱ Determined using EPA Method 9010.

Similar compounds were found in all of the tars, but individual hydrocarbon concentrations varied significantly from one MGP site to another. PAH concentrations ranged from 7,000 mg/kg to 220,000 mg/kg, with various naphthalenes as the dominant components. Several monocyclic aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes (BTEX), and styrene) were also present in concentrations ranging from 13 to 25,300 mg/kg. Much smaller amounts of nitrogen- and sulfur-containing aromatic hydrocarbons (e.g., carbazole and dibenzothiophene) were also found.

It is important to recognize that less than 40% (on a mass basis) of the coal tar constituents can be quantified (see Table 2-2) using common extraction and chromatographic techniques. The unidentified tar fraction is often referred to as the "pitch" for operational purposes. Current sophisticated analytical techniques still lack the capability needed to identify most of the pitch constituents; however, their general nature may be surmised based on coal composition (e.g., Whitehurst et al., 1980) or oil composition. A majority of the pitch constituents are aromatic compounds with high molecular weights and low aqueous solubilities; thus, they may not be of direct concern in terms of groundwater contamination. However, the physical and chemical characteristics of the pitch may exert a strong influence on the rates of release and the equilibrium partitioning of the more-soluble tar constituents (e.g., BTEX, naphthalenes) that are of greater environmental concern. Also, nitrogen- and sulfur-containing aromatic hydrocarbons present in coal tars may impart nonideal behavior.

Tar-Water Partitioning

The relative success in applying a model based on Raoult's law convention for gasolines (Cline et al., 1991), diesel fuels, and motor oil prompted the investigation of whether ideal behavior could also be assumed for coal tars. Compared to gasolines and diesel fuels, coal tars are compositionally more complex; thus, greater deviations from ideal behavior might be expected. The assumption of ideal behavior for coal tar is postulated here for practical expediency, since it reduces the number of parameters needed to estimate PAH concentrations in groundwater. Ideal behavior is not necessarily expected for such materials, but it is hoped that the assumption will be adequate within a specified acceptance factor; a factor-of-two has been chosen here to be adequate for field-scale applications. Experimental measurements of tar-water partition coefficients are difficult, and are subject to significant errors. Thus, experimental artifacts as a possible cause must be eliminated before attributing nonideal behavior to a given coal tar or even to one or more constituents within a coal tar. It is with this pragmatic perspective that we will interpret tar-water partitioning data. The investigations of tar-water partitioning involved analysis of data collected in this study for eight tars, analysis of published data, and theoretical analysis of solute-solute interactions that might lead to nonideal behavior.

Analysis of Laboratory Data

The tar-water partitioning data for the eight tars examined in this study are presented in Figures 2-2 through 2-5. The logarithm of the average K_{tw} value and the calculated standard deviations are shown along with the prediction based on Eq.

(2-6) (solid line) and the factor-of-two tolerance intervals. For most coal tars, the data points are scattered about the ideal line within the factor-of-two bounds suggesting that the assumption of ideal behavior suffices (again, within a factor-of-two error) in predicting K_{tw} for the PAHs. For the one exception (ID# 1), measured data points lie consistently above the ideal line (Figure 2-2A) indicative of an error in the estimate of the molar volume. Specific causes for the systematic deviation observed with coal tar ID# 1 need to be further explored.

Benzo(a)anthracene is the only PAH that consistently lies substantially below the ideal line for most of the coal tars. Uncertainties arising from both analysis and parameter estimation may have resulted in the observed negative deviations. Analysis of benzo(a)anthracene in the aqueous phase approached detection limits, thus contributing to uncertainties. A greater source of error was probably incurred in the estimation of the supercooled liquid solubility for benzo(a)anthracene. The S_f values (given in Table 2-1) used in plotting $\log K_{tw}$ values in Figures 2-2 through 2-5 were estimated assuming a constant entropy of fusion (ΔS_f) (Yalkowsky, 1979). For most compounds, this method may be preferred over attempts to find reliable measured ΔH_f values needed for a direct calculation. However, in the case of benzo(a)anthracene the S_f values estimated using the average ΔS_f value was about one order of magnitude higher than that calculated using the ΔH_f value reported by Chio et al. (1985). Thus, the reasons for the observed deviation of benzo(a)anthracene data points from the ideal line are indeterminate.

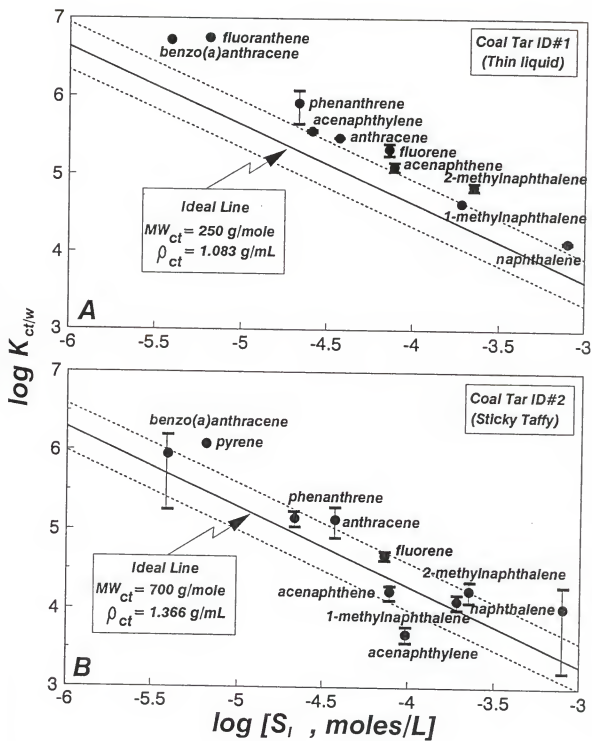


Figure 2-2. Comparison of measured tar-water partition coefficients ($K_{w,w}$) and predictions based on Raoult's law for ID# 1(A) and ID# 2(B) coal tars.

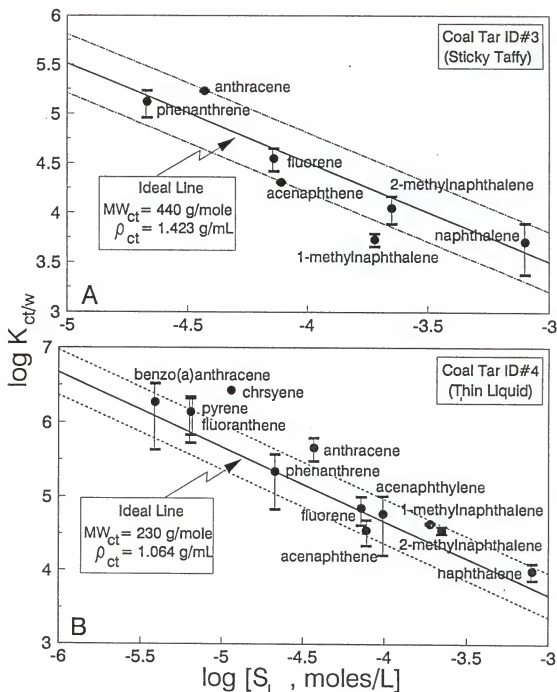


Figure 2-3. Comparison of measured tar-water partition coefficients (K_{tw}) and predictions based on Raoult's law, for ID# 3(A) and ID# 4(B) coal tars.

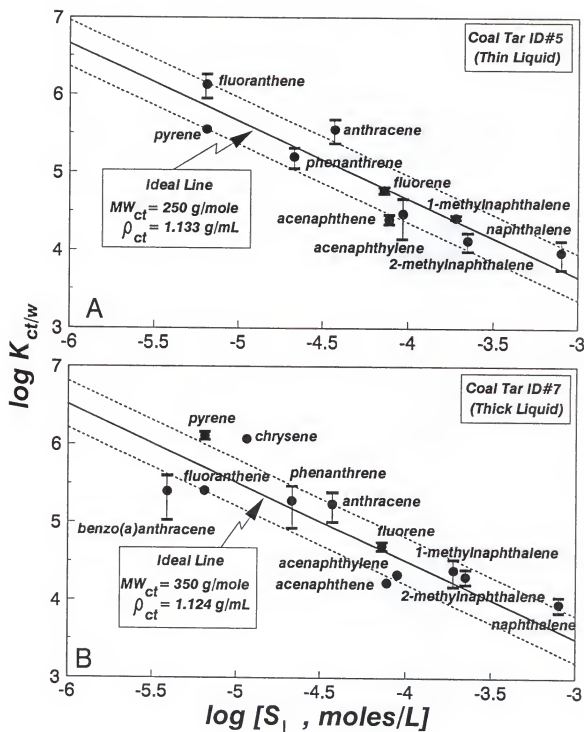


Figure 2-4. Comparison of measured tar-water partition coefficients (K_{tw}) and predictions based on Raoult's law, for ID# 5(A) and ID# 7(B) coal tars.

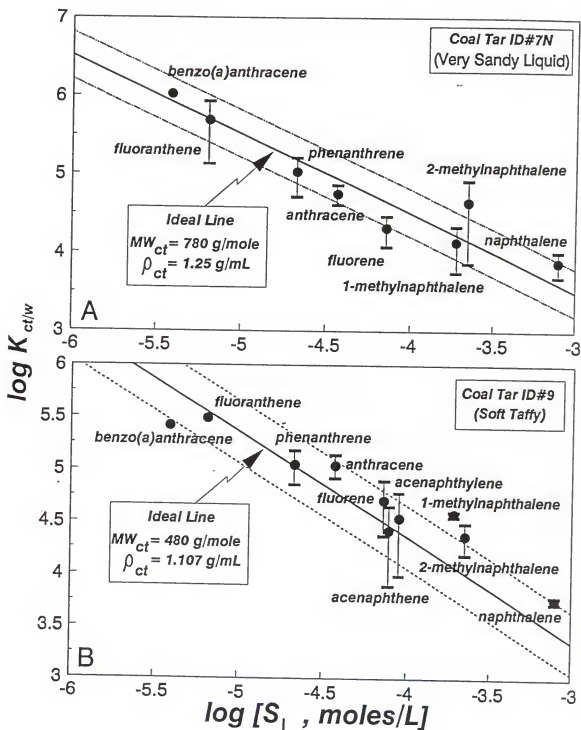


Figure 2-5. Comparison of measured tar-water partition coefficients ($K_{ct/w}$) and predictions based on Raoult's law, for ID# 7N(A) and ID# 9(B) coal tars collected by EPRI.

Analysis of Literature Data

The tar-water partition coefficients (K_{tw}) for several PAHs compiled from the literature (Rostad, 1985; Groher, 1990; Picel, 1988) for three different coal tars, are plotted in Figure 2-6 in a manner similar to Figures 2-2 through 2-5. For each coal tar, the ideal line (solid line) shown was calculated from Eq. (2-6) using the best estimates available for MW_{ct} and ρ_{ct} . For the coal tar investigated by Rostad et al. (1985) (Figure 2-6A), the ideal line was calculated using the ρ_{ct} reported and a MW_{ct} value estimated from a weighted average of the mole fraction and molecular weight of each known component. For the unknown fraction, an average molecular weight of 300 g/mole was assumed. Picel et al. (1988) reported values for both ρ_{ct} and MW_{ct} . Groher (1990) did not report values for MW_{ct} and ρ_{ct} ; therefore, data for a coal tar, similar in composition, obtained from the same site a few years later was used to estimate the ideal line (Figure 2-6B).

For most of the PAHs, the measured K_{tw} values are within a factor-of-two from the ideal line, with the best agreement observed for the Picel et al. (1988) data (Figure 2-6C). Observed deviations from the ideal line could be the result of considerable nonideality in the tar-water system or a consequence of various experimental artifacts including inadequate time for equilibration and poor recovery of the PAH from the aqueous phase. The probability of such experimental artifacts increases for the larger PAHs where a greater difficulty is often encountered in accurately measuring the solubility of rather insoluble compounds.

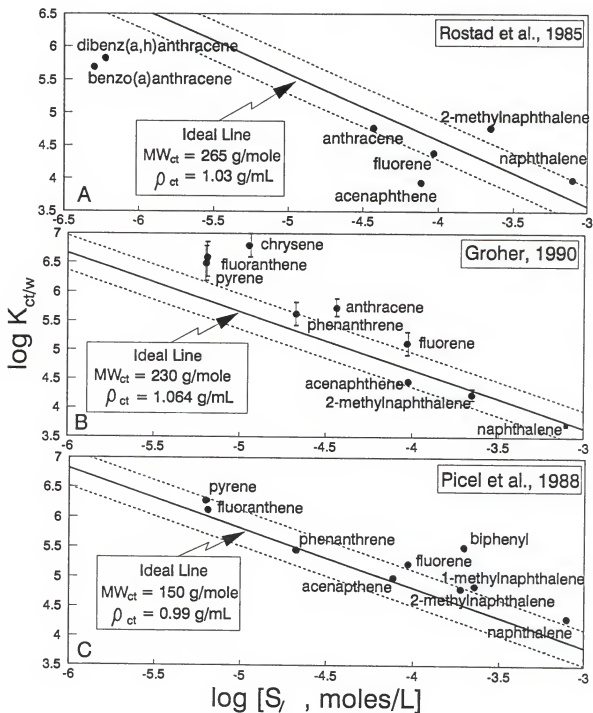


Figure 2-6. Comparison of measured tar-water partition coefficients ($K_{t/w}$) reported in the literature and predictions based on Raoult's law. Literature source as indicated.

A decrease in the measured K_{tw} values would be anticipated for deviations resulting from sufficient nonideality as observed in Figure 2-6A for the Rostad et al. (1985) data. The expectation of the presence of nonideality resulting in negative deviations for PAHs is based on work by Chiou and Schmedding (1982) and Chio et al. (1985) where the activity coefficients of several PAHs were measured in water-saturated octanol and mixtures of benzene and cyclohexane. In both cases, the activity coefficient of a given PAH in the organic phase (γ_o^*) were found to be greater than unity. Values of γ_o^* greater than unity will result in $\log K_D$ values smaller than those estimated assuming ideal behavior.

Predicting Aqueous-Phase PAH Concentrations

Coal Tars

The $\log K_{tw}$ versus $\log S_i$ relationship observed for several coal tars (Figures 2-2 through 2-5) suggests that the application of Raoult's law and the assumption of ideal behavior may be adequate to predict the concentration of PAHs in groundwater (C_w) in contact with a coal-tar source. Equation (2-3) was used to estimate the concentrations of several PAHs expected to be present in a groundwater in equilibrium with a coal tar were estimated using Eq. (2-3) for the coal tars investigated. The mole fraction of the PAH in the organic phase (x_o) needed in Eq. (2-3) was approximated by the product of the mass fraction (mg/g) in the coal tar and MW_{ct} (i.e., $C_w = M_i MW_{ct} S_i$). A log-log plot comparing predicted aqueous concentrations (converted to commonly reported units of mg/L) and those measured during the laboratory partitioning studies is shown in Figure 2-7. The error bars

shown in Figure 2-7 for the laboratory-measured concentrations represent the standard errors calculated from replicate averages. An arrowhead on an error bar indicates that the lower bound approached the limit of detection. For the predicted concentrations, the error bars shown in Figure 2-7 were estimated from the standard errors calculated from the replicate average of M_i . Also given in Figure 2-7 is the ideal line (i.e., 1:1 correlation) with the corresponding factor-of-two tolerance intervals.

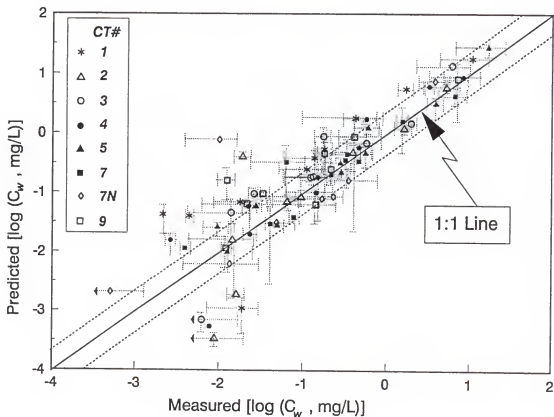


Figure 2-7. Comparison of laboratory-measured aqueous-phase concentrations (C_w) with those predicted on the basis of Raoult's law for eight coal tars.

Confidence in the C_w values predicted using Eq. (2-3) is dependent on several factors other than the premise of ideal behavior, including uncertainty about the input parameters (e.g., M_i , MW_{ct} , and S_i). Both M_i and MW_{ct} can be determined experimentally; therefore, errors associated with these parameters can be obtained from replicate analysis information. Sampling and chromatographic analysis of this heterogeneous liquid waste is prone to considerable errors; therefore, the deviation associated with M_i is probably the greatest source of error in estimating C_w values.

A majority of the data presented in Figure 2-7 lie within the factor-of-two intervals given about the 1:1 correlation. The data that lie outside the factor-of-two intervals result in predicted concentrations greater than those measured, with the exception of the data points below the 1:1 correlation which correspond to benzo(a)anthracene. Benzo(a)anthracene is present in small amounts in coal tar, thus often approaching the limits of analytical detection. In addition, aqueous solubility measurements for compounds with small values (i.e., $<10^{-2}$ mg/L) become increasingly less reliable. Good agreement for a majority of PAHs within a factor-of-two suggests that the use of Eq. (2-3), based on Raoult's law, may be adequate for estimating PAH concentrations. At the very least, aqueous concentrations estimated using this approach should be considered more appropriate and definitive than merely assuming crystal solubilities for aqueous-phase concentrations.

Given the variations that may exist in (1) the different coal tar deposits at a given site, and (2) the extent of weathering at that site, it would be advantageous to estimate maximum PAH concentrations that might be found at any site. In order to

estimate maximum C_w values, the eight coal tars investigated were assumed to be representative of coal tars that might be found at any site in the United States. The maximum concentrations of the PAHs investigated based on the data compiled for the eight coal tars, are given in Table 2-3 along with the ratios of C_w to S_w . Note that the maximum C_w expected is the crystal aqueous solubility for anthracene, chrysene, and benzo(a)anthracene.

Table 2-3. Maximum C_w values for several PAHs based on the data compiled for eight coal tars.

Compound	S_w (mg/L)	Maximum C_w^a	C_w/S_w
Naphthalene	32	14 ^b	0.44
1-methylnaphthalene	27	2	0.05
2-methylnaphthalene	26	1.4	0.05
Acenaphthylene	3.93	0.5	0.13
Acenaphthene	3.42	0.3	0.1
Fluorene	1.9	0.3	0.16
Phenanthrene	1.0	0.4	0.3
Anthracene	0.07	S_w	1.0
Fluoranthene	0.27	0.01	0.4
Pyrene	0.16	0.1	0.5
Benzo(a)anthracene	0.0057	S_w	1.0
Chrysene	0.006	S_w	1.0
Benzo(a)pyrene	0.0038	0.001	0.3

^a T=25°C

^b Result from data compiled for seven of the eight coal tars; data for one tar resulted in a prediction of 26 mg/L.

In the absence of cosolvents and other solubility-enhancing adjuvants (e.g., dissolved organic carbon, surfactants, etc.), the maximum aqueous-phase concentration (C_w) is limited by the crystal solubility (S_w). Although the hypothetical supercooled liquid solubility is used to obtain best estimates for C_w , mixing of the chemical with the aqueous phase is ultimately governed by interactions with the solvent. These are expressed through the crystal solubility (S_w) (Pinal, 1988). For a PAH that has a low aqueous solubility, high melting point, and is present in high concentration in the coal tar, the concentration predicted in the aqueous phase assuming ideal behavior would be the crystal aqueous solubility (S_w).

Diesel Fuels

Reasonable agreement shown previously in the predicted and measured $\log K_{dw}$ versus $\log S_i$ relationships for most PAHs (Figure 2-1) also supports the use of Raoult's law in predicting maximum PAH concentrations that may be present in the aqueous leachate leaving a diesel-fuel contaminated area. Using Raoult's law and assuming ideal behavior, the concentration of a constituent in the aqueous phase in equilibrium with the organic phase is proportional to the mole fraction of that constituent in the organic phase (see Eq. 2-3). Substituting Eq. (2-5) into Eq. (2-1) gives the following equation for the equilibrium aqueous-phase concentrations:

$$C_w = \frac{C_{df} MW_{df} S_i}{P_{df}} \quad (2-7)$$

where the subscripts df and w refer to diesel fuel and water, respectively. In Figure 2-8, PAH concentrations predicted using eq 2-7 were converted to commonly reported units ($\mu\text{g/L}$) and plotted against concentrations measured in the laboratory partitioning studies with the four diesel fuels.

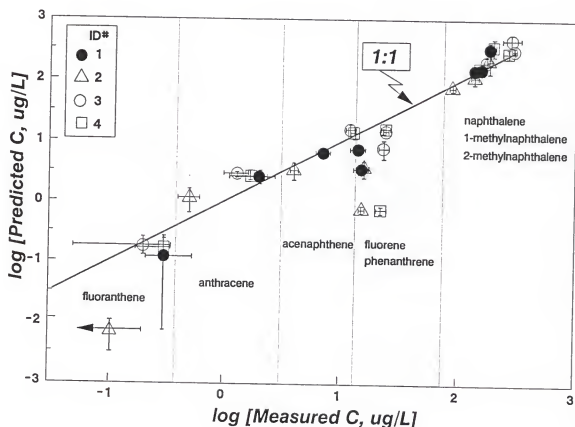


Figure 2-8.

Comparison of laboratory-measured aqueous-phase concentrations ($C_w, \mu\text{g/L}$) with those predicted on the basis of Raoult's law for four diesel fuels.

Also included in Figure 2-8 are the confidence intervals for both the measured and predicted concentrations. Measured concentration errors were estimated from the standard deviations observed in triplicate analyses of the aqueous phase; confidence intervals with arrows reflect limits of detection. Similarly, the errors associated with the predicted values were estimated from the standard deviations obtained from triplicate analyses of the neat diesel fuel, i.e., the determination of C_{df} . The confidence intervals given for the predicted C_w in Figure 2-8 did not include errors incurred in estimating MW_{df} or ρ_{df} . Overall, the correspondence between measured and predicted equilibrium aqueous phase concentrations shown in Figure 2-8 is to be very good.

Assessment of Deviations from Ideal Behavior for Equilibrium Conditions

The relationship between K_d and S_i assumed previously (el 2-6) was based on the simplifying assumption of ideal behavior (i.e., $\gamma_o^* = 1$ and $\gamma_w^* = \gamma_w$). Several factors may cause deviations from the assumed ideal behavior for diesel-water partitioning of PAHs. For example, negative deviations from the ideal line could result from the presence of surfactants or emulsions or sufficient nonideality, while positive deviations can be expected if equilibrium has not been reached, and apparent deviations (positive or negative) can result from uncertainty in parameter estimation.

For a mixture which is complex in composition and behaves in a "nonideal" fashion, the partition coefficient (K_d) between an organic liquid and an aqueous phase can be related to the aqueous solubility of the pure liquid (S_i) in the following

manner (Chiou and Schmedding, 1982):

$$\begin{aligned} \log K_d = & -\log S_l - \log \left(\frac{MW_o}{P_o} \right) \\ & - \log \gamma_o^* + \log \left(\frac{\gamma_w^*}{\gamma_w} \right) \end{aligned} \quad (2-8)$$

Comparison of Eqs. (2-6) and (2-8) suggests that any deviations due to nonideal behavior will arise from the last two terms on the right hand side of Eq. (2-8). Banerjee (1984) observed that the presence of other components in the aqueous phase had a minimal effect on solute activity; therefore, it was assumed that $\gamma_w^*/\gamma_w = 1$, thus requiring only estimates of γ_o^* . The UNIFAC model UNIFAC (UNIQUAC Functional-Group Activity Coefficient) model proposed by Prausnitz et al. (1980) for estimating activity coefficients in liquid-liquid equilibria was employed to estimate γ_o^* values needed in Eq. (2-8). In this model, a mixture of different chemicals is treated as a mixture of functional groups constituting the components of the mixture. Interactions between functional groups in the mixture, and the likely nonidealities resulting from such interactions, are calculated in order to estimate the activity coefficient of a chemical for a specified phase. Interaction parameters required in the UNIFAC model were obtained from the most current update (Hansen et al., 1991).

A schematic representation of Eqs. (2-6) and (2-8) is shown in Figure 2-9 as a plot of $\log K_D$ versus $\log S_l$. Note that the expected relationship for an ideal mixture is depicted by the solid line, with a unit slope and the intercept given as the

$\log \bar{V}_o$ (see Eq. 2-8). The single data point represents a possible value for a solute partitioning between a hypothetical nonideal mixture and water. Note that the magnitude of deviation from the ideal line is given by the last two terms on the right hand side of Eq. (2-8) plus an error term, ϵ , representing experimental uncertainty.

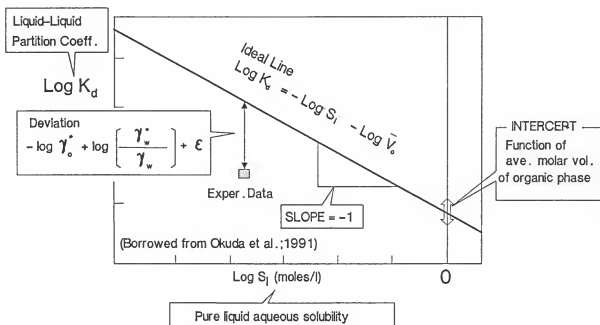


Figure 2-9. Schematic representation of the ideal behavior (Raoult's law) and nonideality in liquid-liquid partitioning.

Application of the UNIFAC model for assessing the potential for nonideality is presented for a gasoline, diesel fuel, and coal tar. Using the UNIFAC model, activity coefficients (γ_o^*) of several aromatic compounds were estimated for an unleaded gasoline simulated to represent the relative compositions (see inset in Figure 2-10) reported in Cline et al. (1991).

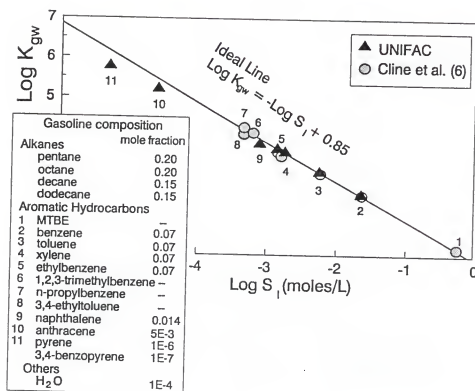


Figure 2-10. $\log K_{gw}$ values for several aromatic hydrocarbons resulting from UNIFAC model calculations and the average \log_{gw} values experimentally determined by Cline et al. (1991) plotted against $\log S_1$ values along with the ideal line based on Raoult's law.

The estimated γ_o^* values were then used to predict $\log K_{gw}$ values (shown as solid triangles in Figure 2-10) according to Eq. (2-8). UNIFAC model calculations for the monocyclic aromatic compounds represented in Figure 2-10 (compounds 2-5) confirm the experimental observations of Cline et al. (1991) that gasoline-water partition coefficients of several liquid hydrocarbons can be approximated by assuming ideal

behavior. However, for compounds with increasingly more aromaticity and are solids in their standard state (PAH compounds 9-11 in Figure 2-10), the UNIFAC model predicted some negative deviation from ideal behavior. Partition coefficients for these compounds were not measured by Cline et al. (1991) as they are present only in small quantities in gasoline. Compared to gasolines, diesel fuels contain a larger fraction of low-solubility PAHs. Therefore, it was of interest to see if the UNIFAC model estimations of γ_o^* for these PAHs resulted in deviations from ideality.

The composition of the diesel fuel assumed in the UNIFAC model calculations is shown in Figure 2-11. The concentrations of the eight PAHs chosen were comparable to those found in the diesel fuels used in this investigation; the concentrations of monocyclic aromatic hydrocarbons used were based on analyses reported by Thomas and Delfino (1991); and the mole fraction of water was selected based on the maximum ASTM limiting requirement for diesel fuel (Kirk-Othmer, 1980). To simulate the alkane fraction of the diesel fuel, a representative compound for each alkane (n-, iso-, and cyclo-alkane) was selected (see Figure 2-11) in proportion to those reported by Mackay et al. (1985). The UNIFAC model calculations for the γ_o^* values of the PAHs ranged between 0.99 for toluene to 1.16 for fluoranthene. The close proximity of the calculated $\log K_{dw}$ values (solid triangles in Figure 2-6) to the ideal line based on Raoult's law for the simulated diesel fuel suggest that deviations from ideal behavior for PAHs smaller than fluoranthene may be negligible. These calculations suggest that deviations from the ideal line for the larger PAHs noted in Figure 2-1 cannot be attributed to solute-solute interactions,

lending support to analytical sources of error for the observed deviations. Independently assessing the potential for nonideal behavior emphasizes the need to account for experimental and analytical sources of errors when judging whether the deviation noted from the ideal line is indeed the result of nonideal behavior.

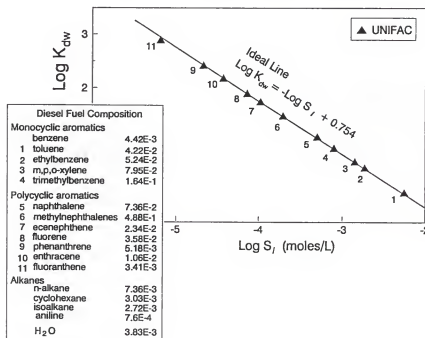


Figure 2-11. $\log K_{dw}$ values for several aromatic hydrocarbons resulting from UNIFAC model calculations plotted against $\log S_i$ values along with the ideal line based on Raoult's law.

Based on the success for gasoline and diesel fuel, an attempt was made to use the UNIFAC model to assess the likelihood of nonideality for coal tar ID#4. Since less than 40% of the composition of this coal tar was unknown (as usually is the case), it was represented by a single compound indicated in Figure 2-12. The UNIFAC model simulations suggested that nonidealities are indeed small, and that

Raoult's law approximation was justified (Figure 2-3). A note of caution is in order, however, the UNIFAC model results depend heavily on the presumed composition of the pitch (62% mole fraction in our example with coal tar ID#4), and on the presence of polar constituents in coal tar (none were present in significant quantities in this example).

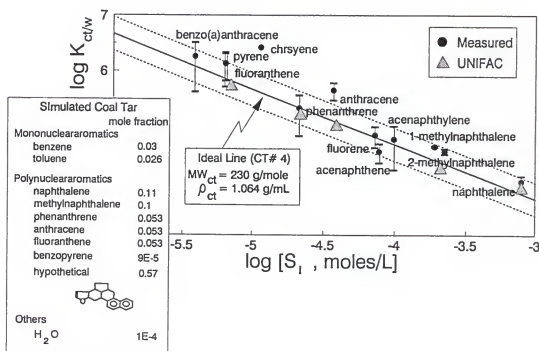


Figure 2-12. Comparison of measured and predicted tar-water partition coefficients for several PAHs: Raoult's law (solid line) and UNIFAC model (solid triangle).

Summary

Release of aromatic hydrocarbons from an immiscible organic liquid waste is governed primarily by solubility phenomena. In assessing the likelihood of soil and water contamination from complex organic wastes (e.g., gasoline, diesel fuel, and coal tar), it is incorrect to assume that PAH concentrations in groundwater would be equal to the corresponding aqueous solubilities of the pure compounds. Such an assumption usually leads to considerable over-predictions of the PAH concentrations likely to be found in groundwater.

According to the model based on Raoult's law, the concentration of an organic constituent in the aqueous phase in equilibrium with an "ideal" organic mixture is proportional to the mole fraction of that constituent in the organic phase. An experimental evaluation of a model based on ideal behavior was presented for the partitioning of aromatic hydrocarbons from diesel fuel and coal tar into water, and the results compared to data reported earlier for gasoline/water and motor oil/water partitioning. The diesel fuel/water and tar/water partitioning of several PAHs, all solids in their standard state, was well described within a factor of four for diesel fuels, and within a factor of two for coal tars by employing supercooled liquid solubilities and assuming ideal behavior. Good agreement between the observed partitioning of several PAHs and UNIFAC model calculations for a simulated gasoline, diesel fuel, and coal tar further suggests that the extent of deviations from ideal behavior may be relatively small.

Agreement between the model predictions based on Raoult's law and measured liquid-liquid partitioning data for several aromatic hydrocarbons is not to be taken as evidence that such compositionally-complex organic liquid wastes are

indeed ideal mixtures. Rather, the assumption of ideal behavior might suffice for practical considerations in providing first-order estimates for maximum PAH concentrations likely to be found in groundwater leaving an area contaminated with residual OILs. Several site-specific hydrogeologic factors might lead to significant mass transfer constraints for solute partitioning. Such factors include: random spatial variability in aquifer hydraulic properties, the patterns of residual fuel entrapment, and the source of fuel contamination (e.g., surface spill versus subsurface leaks). Under nonequilibrium mass transfer conditions, the concentrations of organic constituents detected in groundwater are likely to be smaller than those estimated using the equilibrium approach presented here. In contrast, larger concentrations might be observed in the presence of surfactants, emulsifiers, or cosolvents.

CHAPTER 3

COSOLVENT EFFECTS ON SORPTION OF ORGANIC ACIDS BY SOILS FROM METHANOL/WATER SOLUTIONS

Introduction

The codisposal of contaminants, as well as the potential use of alternative fuels and mixing of contaminant plumes from different sources, will result in environmental contamination problems consisting of a complex mixture of chemicals including both polar and nonpolar organics in miscible and immiscible solvent mixtures. Solubility, sorption, and transport of hydrophobic organic compounds (HOCs) are well characterized in aqueous solutions and various complex mixtures. Solubility of HOCs increases with increasing volume fraction cosolvent of an organic cosolvent (Yalkowsky and Roseman, 1981; Yalkowsky, 1985; 1987; Rubino and Yalkowsky, 1987a; 1987b; Fu and Luthy, 1986; Pinal et al., 1990; 1991). Sorption of HOCs is inversely related to solubility and as a result, an increase in solubility from the addition of a cosolvent leads to a proportional decrease in sorption (Rao et al., 1985; 1990; Nkedi-Kizza et al., 1985; 1987; Rao and Lee, 1988; Woodburn et al., 1986; Fu and Luthy, 1986).

For hydrophobic ionizable compounds (HIOC) of environmental interest, data on solubility, sorption, and transport in mixed solvents are limited. Some research investigating the impact of multiple solutes on HIOC sorption (i.e.,

competitive sorption) by soils from aqueous solutions has been documented (Felice et al., 1985; Zachara et al., 1987; Rao and Lee, 1987); however, little attention has been given to the behavior of HIOCs in solvent mixtures.

Pharmaceutical literature contains solubility data for several drugs spanning a wide polarity range. As shown in Figure 3-1, Yalkowsky and Roseman (1981) observed that as solute polarity increases relative to the solvent, cosolvency curves become increasingly more parabolic in shape until an inverse relationship occurs (i.e., decreased solubility with cosolvent additions). Such behavior is explained on the basis of the solute-solute and solute-cosolvent interactions. Therefore, for compounds that exhibit a decrease in solubility with addition of a cosolvent ($\log K_{ow} < 1$), sorption may increase with increasing cosolvent composition.

For the sorption of naphthol, quinoline, and dichloroaniline by three different soils from methanol/water and acetone/water solutions up to 50% by volume, Fu and Luthy (1986b) observed log-linear behavior inversely proportional to corresponding solubility data (Fu and Luthy, 1986a) as observed with HOCs. Similar behavior was observed by Zachara et al. (1986) for quinoline sorption by a natural clay isolate and montmorillonite in binary mixtures of methanol or acetone and water regardless if the protonated or neutral species predominated in solution. For these HIOCs it appears that the cosolvent effect on sorption is dominated by solvation forces (i.e., solubility) similar to that observed with HOCs even though sorption mechanisms for HIOCs and HOCs are different (electrostatic and ion exchange versus hydrophobic partitioning).

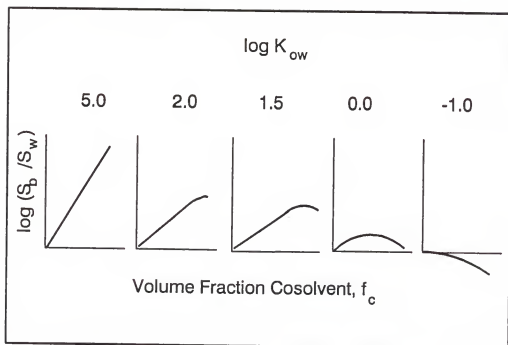


Figure 3-1. Schematic representation of cosolvency plots for solutes with a range of $\log K_{ow}$ values.

For an acidic fluorescent dye (Rhodamine WT) in binary mixtures of methanol/water and acetone/water at cosolvent fractions above 30%, sorption was observed to increase even though at lower cosolvent fractions ($\leq 30\%$) sorption appeared to follow an inverse log-linear relationship (Soerens and Sabatini, 1992). Previous use of Rhodamine WT as a surface and groundwater tracer prompted an investigation on the potential use of this dye as a tracer in alternative fuel research (i.e., alcohol-based fuels). In soil thin-layer chromatography (TLC) studies (Hassett et al., 1981), the herbicide dicamba (3,6-dichloro-2-methoxybenzoic acid) moved with the solvent front in both aqueous and 50/50 (v/v) ethanol/water solutions, but was strongly retained by soil with neat ethanol as the mobile phase.

For analysis of various carboxylic acids and substituted phenols by reversed-phase chromatography using an acidified mobile phase (i.e., when neutral species dominate), retention is inversely proportional to cosolvent content as observed for HOCs. Lewis and Wilson (1984) observed similar behavior for several carboxylic acids in non-acidified methanol/water solutions (0 to 80%) using reversed-phase TLC plates impregnated with an ion-pairing agent tetra-n-butylammonium bromide (TBA). However, in the absence of an acidified mobile phase or an ion-pairing reagent, cosolvent effects were minor. These data suggest that the retention behavior of organic acids by a hydrophobic surface is similar to HOCs only when the charge is compensated (e.g., neutral by protonation or paired with a counterion).

In considering the impact of cosolvents on sorption, the following interactions must be considered: solute-solute; solvent-solvent; solvent-solute, solvent-sorbent, and solute-solvent-sorbent interactions. The first three pairs of interactions can be assessed from solubility studies. For HOCs, solute-solute interactions are ignored due to the absence of both specific functional groups and high solute concentrations. For most miscible solvents (e.g., alcohols), irregular behavior due to specific complexation of solvent and water molecules doesn't appear to be of concern. For sorption of HOCs, solvent-solute interactions, as described by solubility, are found to predominate such that the impact of solvent-sorbent interactions have been considered minor. However, for solutes containing specific functional groups, the impact of the cosolvent on the sorbent may have considerable impact.

For HIOCs, the impact of adding a cosolvent to aqueous solutions on the conditional ionization constant of a HIOC must be considered. Likewise, similar impacts on the ionization of sorbent functional groups and subsequent solute-sorbent interactions must also be considered. Also, the impact of solvent-water interactions that were considered negligible in predicting HOC behavior may be of importance in understanding the chemodynamic behavior of HIOCs, as well as the different propensities of the cosolvent and water to hydrate both the solute and the sorbent.

Cosolvent-induced interactions involving the sorbent surface include: speciation of organic matter functional groups, clay surface acidity, and ion-association with the surface. Both acidic and basic groups tend to become neutral with increasing cosolvent content as a result of shifts in the pK_a' (Perrin et al., 1981), leading to a net increase in hydrophobicity of soil organic matter. This phenomenon may explain why decreases in HOC sorption with increasing f_c are smaller in magnitude than would be predicted from solubility profiles in mixed solvents (Rao et al., 1990; Nkedi-Kizza et al., 1985; 1987; Rao and Lee, 1988). Parallel to changes in pK_a' , Kan and Tomson (1990) observed a decrease in naphthalene sorption by Lincoln fine sand from aqueous solutions by increasing pH (pK_a fixed, but pH varied). However, the increase in sorption resulting from such changes on surface hydrophobicity are likely to be more than compensated by cosolvency effects.

The presence of cosolvents may also alter the surface acidity of the clay fraction. Loeppert et al. (1977, 1979) found that the amount of base required to titrate the pH-dependent sites of kaolinite varied in the following manner: methanol

\leq water < DMSO < acetonitrile. The fact that larger titers in DMSO and acetonitrile were required was attributed to (1) pH-dependent sites for which a quantitative endpoint was not obtained in aqueous media due to the acidic properties of water, and (2) increased surface acidity in organic solvents. Loeppert et al. (1986) also observed an increase acidity of montmorillonite in acetonitrile and dimethylformamide. No apparent changes were observed in surface acidity with neat methanol (Loeppert et al., 1979). Similar conclusions were made by Hesleitner et al. (1991), who noted that addition of methanol ($f_c \leq 0.5$) caused no apparent change in the surface charge density of a hematite surface (iron oxide) or in the point of zero charge which coincided with the isoelectric point.

Cosolvent-enhanced formation of ion-pairs with positive charges on the sorbent surface may cause an increase in sorption of organic acids with addition of an organic cosolvent even if solubility increases. As previously mentioned, Hesleitner et al. (1991) observed no changes in the total surface charge of hematite in the f_c range investigated ($f_c \leq 0.5$), but noted a pronounced decrease in electrokinetic potentials with increasing methanol fractions (i.e., effective surface charge was lowered). They attributed the decrease in electrokinetic permittivity to an enhancement of counterion association with the surface charged groups. This counterion association could include both the formation of outer-sphere complexes by bridging of the carbonyl to the solvent (water and/or cosolvent) coordinated on the exchange cation (Farmer and Russell, 1967) and inner-sphere complexation by hydrogen bonding of the carbonyl group with protonated hydroxyls on the surface

(Kohl and Taylor, 1961; Stumm et al., 1980). These mechanisms have been included among those proposed in the literature for sorption of organic acids in aqueous solutions (Farmer and Russell, 1967; Kohl and Taylor, 1961; Stumm et al., 1980; Davis, 1982; Kummert and Stumm, 1980); however, the impact of cosolvents on such interactions has yet to be investigated.

In this chapter, the overall impact of methanol additions on (1) the enhancement of solute-solvent interactions as described by solubility; and (2) speciation changes due to cosolvent induced changes in the solute's pK_a will be assessed for the sorption of several organic acids by soils. Subsequent chapters will assess (1) speciation changes due to changing pH at several fixed methanol/water compositions for benzoic acid and PCP sorption; (2) the overall impact of several solvents with a wide range in solvent properties on the sorption of benzoic acid; and (3) the relationship between solute properties, such as acidity and hydrophobicity, on the shapes of the sorption curves observed in methanol/water solutions.

Theory

The following log-linear model successfully describes (Yalkowsky and Roseman, 1981; Fu and Luthy, 1986; Pinal et al., 1990; Rao et al., 1985; Nkedi-Kizza et al., 1985, 1987; Rao and Lee, 1988; Woodburn et al., 1986) solubility and sorption of HOCs in miscible solvent-water systems,

$$\log S_b = \log S_w + \sigma f_c \quad (3-1)$$

$$\log(S_c/S_w) = \sigma \quad (3-2)$$

$$\log K_b = \log K_w - \alpha \sigma f_c \quad (3-3)$$

where S is solubility (mg/L), K is sorption coefficient (mL/g) with subscripts b , c , and w referring to binary mixtures, pure cosolvent, and water, respectively; f_c is volume fraction cosolvent; σ describes the cosolvency power of a solvent for a solute; and α accounts for solvent-sorbent interactions.

Sorption of HIOCs is dependent on the formation of neutral and ionized species, as determined by pH and the solute acid dissociation constant (pK_a). For many organic acids, the neutral species is sorbed more than its dissociated (anionic) species, and the differences in the sorption coefficient values can be rather large. Thus, the measured sorption coefficient for HIOCs is a strong function of pH and conditional dissociation constants (pK_a') of the solute in the solvent system of interest. Lee et al. (1990) showed that the pH-dependence of pentachlorophenol (PCP) sorption from aqueous solutions can be described by,

$$K = K_{w,n} \phi_n + K_{w,i} (1 - \phi_n) \quad (3-4)$$

where

$$\phi_n = (1 + 10^{pH - pK_a'})^{-1} \quad (3-5)$$

and subscripts n and i refer to neutral and ionized species, respectively. Similar findings for the sorption of several other organic acids by various sorbents have been reported in the literature (Jafvert, 1990; Kukowski, 1989; Fontaine et al., 1991).

If solubility of a solute increases with addition of a cosolvent to an aqueous solution (see Figure 3-1), a decrease in sorption is expected. Also, the addition of a solvent with a low dielectric constant will result in an alkaline shift in the pK_a of an organic acid (Perrin et al., 1981), leading to an increase in the fraction of neutral species. In the absence of specific adsorption reactions, the neutral species will be sorbed to a greater extent. Therefore, the addition of a cosolvent brings about two opposing effects. To incorporate both speciation and cosolvent effects, Eq. (3-1) and Eqs. (3-3, 3-4, and 3-5) were combined,

$$K_b = K_{w,n} \phi_n \beta_n + K_{w,i} (1 - \phi_n) \beta_i \quad (3-6)$$

where

$$\beta_n = 10^{-\alpha_n \sigma_n f_c}; \quad \beta_i = 10^{-\alpha_i \sigma_i f_c} \quad (3-7)$$

The cosolvency power for the neutral species (σ_n) will increase relative to hydrophobicity. The cosolvency power for the ionized species (σ_i) will be a function of the relative hydrophobicity of the anion and the potential for ion-pairing. For example, Lee et al. (1990) observed a log-linear decrease in sorption of PCP by Webster soil in methanol/water (0.01 N CaCl_2) solutions ($f_c = 0$ to 40%) for both the neutral species ($\text{pH} < 3$) and ionized species ($\text{pH} < 9$) with resulting values for $\alpha_i \sigma_i$ and $\alpha_n \sigma_n$ were 2.56 and 3.88, respectively. The decrease in sorption observed with

increasing f_c for pentachlorophenolate was attributed to the relatively large hydrophobicity of the anion and the formation of neutral ion-pairs.

Figure 3-2 illustrates the types of cosolvency curves for the sorption of organic acids that might be predicted using Eq. (3-6). Using parameter set #3 results in the presence of primarily the neutral species of the HIOC ($\text{pH}-\text{pK}_a' < -1$) thus yielding cosolvency curves similar to that observed for HOCs (Eq. 3-3). In the absence of specific interactions, a reduction in solubility with increasing cosolvent content might be expected for a solute existing as an anion in solution, thus potentially increasing sorption (parameter set #6). Similar results are predicted using Eq. (3-6) for a solute with relatively small hydrophobicity ($\sigma_n=1$) and assuming no impact of cosolvency on the anionic species ($\sigma_i=0$) (parameter set #2 and #5). Note how the magnitude of the increased sorption predicted by Eq. (3-6) is a function of the inter-relationship between initial soil-solution pH (i.e., $\text{pH}-\text{pK}_{a,w}$) and the σ values. The σ values used in sets #1 and #3 are larger than those used for sets #2 and #5 changing the impact of pH variations. For sets #1 and #3, enhanced linearity and an upward shift is observed with decreasing pH; whereas, for sets #2 and #5, the shape of the sorption curve changes from a convex to a concave shape as pH decreased. Therefore, the overall magnitude and direction of the sorption observed will vary as a function of cosolvency power (σ), soil-solution pH, and cosolvent induced shifts in the observed pK_a' .

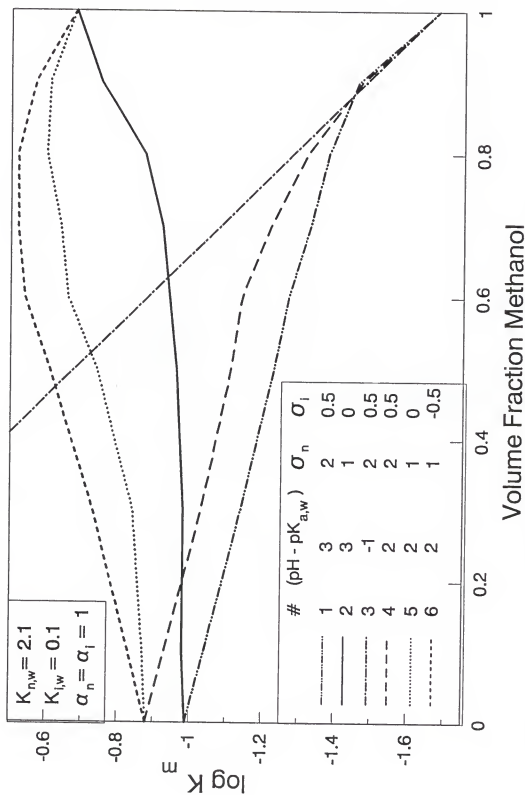


Figure 3-2. Example cosolvency curves that may be predicted by the use of various parameters in Eq. (3-6).

The success of Eq. (3-6) in describing sorption of organic acids is predicated on the ability to measure (or define) the ionization constant (pK_a') and pH in the solutions of interest. Defining pK_a' and pH is fairly straightforward for aqueous systems; however, various complications must be considered for mixed solvent systems. The pH of an aqueous solution is thermodynamically defined as the negative logarithm of the hydrogen ion activity (a_{H^+})

$$pH = -\log a_{H^+} = -\log \gamma_{H^+} [H^+] \quad (3-8)$$

where γ_{H^+} and $[H^+]$ are the hydrogen activity coefficient and concentration, respectively. Experimentally, an electrometric method is usually employed (e.g., pH meter) where the determination of pH is based on the measurement of the electromotive forces (e.m.f.) of standard aqueous buffer solutions. Therefore, the pH of an unknown solution (pH_x) can be determined by

$$pH_x = pH_s + \frac{E_x - E_s}{(RT \ln 10/F)} \quad (3-9)$$

or at $T=298$,

$$pH_x = pH_s + \frac{E_x - E_s}{0.06} \quad (3-10)$$

where E_x and E_s are the e.m.f. values of the solutions, R and F are the gas and Faraday's constants, respectively, and T is absolute temperature. Not shown in Eq. (3-9) are the potentials that arise from the liquid junction and the standard potential of the glass electrode. The difference in these potentials between the standard and

unknown solutions are assumed to be the same when the solution matrix is similar, thus cancelling out in the $(E_x - E_s)$ term.

Likewise, in mixed solvents (denoted by *), pH is thermodynamically defined as

$$pH^* = -\log \gamma_{H^+}^* [H^+] \quad (3-11)$$

If standard mixed solvent buffers are employed, pH can be operationally defined as follows:

$$pH_x^* = pH_s^* + \frac{E_x^* - E_s^*}{0.06} \quad (3-12)$$

It is usually expedient to employ readily available standard aqueous buffers in which case Eq. (3-12) must be modified to estimate the pH of a solution in mixed solvents,

$$pH_x^{app} = pH_s + \frac{E_x^* - E_s}{0.06} \quad (3-13)$$

where pH^{app} is the measured pH of a mixed solvent solution relative to a standard aqueous buffer solution. The differences in the liquid junction potential and the standard potential of the glass electrode between mixed solvents and aqueous solutions cannot be assumed to be the same and must be considered. However, Gelsema et al. (1967) have shown that differences in the standard potentials of the glass electrodes between mixed solvents and aqueous solutions are negligible. The

operational definition of pH for a mixed solvent solution (pH_x^*) referenced to an aqueous standard can then be written as

$$pH_x^* = pH_s + \frac{E_s^* - E_s}{0.06} + \frac{E_{j,x}^* - E_{j,s}}{0.06} \quad (3-14)$$

Therefore, differences in the apparent pH and the actual pH arise from the difference in the liquid junction potentials:

$$\delta = pH_x^{app} - pH_x^* = \frac{E_{j,x}^* - E_{j,s}}{0.06} \quad (3-15)$$

Van Uitert and Haas (1953) achieved a practical standardization of pH measurements in dioxane-water solutions by measuring the pH of a series of HCl solutions of known concentration in the mixed solvents. The difference between the measured pH and the known hydrogen concentration was assumed to be a reasonable estimate for δ . This approach yields estimates for δ that encompass all differences (i.e., liquid junction potential, standard potential, activity, solvent medium effects) observed between a measurement in aqueous versus solvent/water solutions irrespective of the source. The magnitude of δ increases with increasing amounts of an organic solvent. For methanol/water solutions at $f_c \leq 0.8$, δ values are relatively small, but δ values may become greater than 2 as the neat organic solvent is approached (Van Uitert and Haas, 1953; De Ligny and Rehbach, 1960). Although there are obvious shortcomings to this simplified approach, it appears adequate in many cases for estimating pH in several mixed solvent solutions.

Materials and Methods

Sorbents

The primary sorbents used in this study were Eustis fine sand (Psammentic Paleudult) from Florida containing 96.4%, 1.8%, 1.8%, and 0.39% sand, silt, clay, and organic carbon (OC), respectively; and Webster silty clay loam (Typic Haplaquoll) from Iowa (5 miles north and 3 miles east of Ames) containing 30.7%, 42.8%, 27%, 3.0% sand, silt, clay (predominately montmorillonite), and OC, respectively. Specific surface measurements by N_2 -BET of approximately $4 \text{ m}^2/\text{g}$ was obtained for a similar Webster soil subsample used in previous studies (Rao et al., 1988). Both the Eustis and Webster soils were collected from the surface horizon (0-30 cm). The soil OC contents were determined using the Walkley-Black method (Nelson and Sommers, 1982). The soil-solution pH in 0.01 N CaCl_2 was 5.0 and 6.9 for Eustis and Webster soils, respectively. Soils were air-dried and passed through a 2 mm sieve prior to use.

Chemicals

The organic acids used in this study are listed in Table 3-1 along with selected physical and chemical properties. All crystalline compounds had a chemical purity of >98%. All solvents were purchased from J.T. Baker (high purity, HPLC grade) and used without further preparation. For sorption experiments with pentachlorophenol (PCP), ^{14}C uniformly ring-labeled compound was purchased from Sigma Chemical Co. with a specific activity of 12 mCi/mmol and a reported radiochemical purity of >98%.

Table 3-1. Selected Solute Properties

Solute	Melting Point ¹ (°C)	Molecular Weight ¹	pK _a		Aqueous Solubility ³ (mg/L)	Log K _{ow} ³
			Aqueous	Methanol ²		
Pentachlorophenol	190	266.3	4.74 ⁴	8.6	14	5.01
2,4-Dichlorophenol	42	163.0	7.85 ⁴	11.9	4,500	3.23
Picric Acid (2,4,6-trinitrophenol)	121	229.1	0.419 ¹	4.1	14,000	2.03
Gentisic Acid (2,5-dihydroxybenzoic acid)	205	154.1	2.97 ¹	7.6	21,500 ²	NA ⁹
2,4,5-trichlorophenoxy acetic acid	156	255.5	2.8 ⁵	7.4	278	NA
2,4-dichlorophenoxy acetic acid	138	221.0	2.64 ¹	7.6	890	NA
Benzoic Acid	122	122.1	4.20 ¹	9.0	2,900	1.87
Pentafluorobenzoic acid	101	212.1	1.49 ⁶	5.8	NA	NA
Dicamba (3,6-dichloro-o-anisic acid)	115	221.9	1.94 ⁷	6.9	7,900	2.46 ⁸

¹ From Dean (1985); ² This study; ³ From Verschueren (1983); ⁴ From Callahan et al.(1979); ⁵ Koskinen and O'Connor (1979); ⁶ From Walters (1982); ⁷ From Kearney and Kaufman (1976); ⁸ EPA Environmental Fate One-Line Data Base, Version 3.04; ⁹ Not available.

Determination of Ionization Constants

The conditional ionization constants (pK_a') for benzoic acid, gentisic acid, 2,4-dichlorophenoxyacetic acid, PCP, 2,4-dichlorophenol, and dicamba were determined in methanol/water solutions by measuring pH as a function of NaOH additions (Albert and Sergeant, 1984). Solvent mixtures were prepared with 0 to 100% methanol and degassed prior to use. For all solutes except for PCP and dicamba, 0.01 M solutions were titrated with 0.1 M NaOH. For PCP and dicamba, 0.001 M solutions were titrated with 0.01 M NaOH. A Metrohm 686 Titroprocessor, employing a combined pH glass electrode (6.0202.100) and a resistance thermometer (6.1103.000), continuously measured pH and temperature, respectively. The pH meter was calibrated using aqueous buffers. The temperature of the solutions was 24 ± 0.5 C. Titrations were performed in duplicate in 50 mL beakers placed on a stirring plate to mix the solutions. The ionization constants determined in this study are *mixed* ionization constants (Albert and Sergeant, 1987) rather than *true* thermodynamic ionization constants. A brief discussion on the difference between the various ionization constants are given in Appendix B along with sample sets of titration data from this study and corresponding calculations.

In calculating pK_a' values, adjustments for the impact of methanol on pH measurements were made using a method similar to that employed by Van Uitert and Haas (1953) as described above for the measurement of pH in mixed solvents. This method consisted of measuring the pH of 0.001 M hydrochloric acid in the mixed solvent. The difference (δ) between the pH measured in water and in the

mixed solvent was added to the pK_a estimated from the titration curve (i.e., $pK_a' = pK_a + \delta$). From 0 to 70% methanol, δ values were negligible. At higher methanol fractions, δ values were approximately 0.1, 0.4, and 2.3 for f_c values of 0.8, 0.9 and 1.0, respectively. Similar results were obtained by De Ligny and Rehbach (1960) for methanol/water solutions by comparing pH measured in aqueous standard buffers (KCl saturated solutions) and standard buffers prepared in the appropriate mixed solvent using the method proposed by the National Bureau of Standards (Bates et al., 1963). Therefore, the corrections needed to adjust the pK_a determined in mixed solvents relative to the use of aqueous standard buffers are only significant at $f_c \geq 0.9$.

pH of Soil Suspensions in Mixed Solvents

When considering the measurement of pH in mixed solvent soil-suspensions, problems in addition to those previously discussed for pH measurements in mixed solvents arise. It has long been recognized that the ambiguity of measuring the pH in aqueous soil solutions, and even more so in soil suspensions, is due to the inability to accurately determine liquid junction potential differences between standard buffer solutions ($E_{j,s}$) and soil-solutions ($E_{j,ss}$). Even with this ambiguity, the error in the measured pH resulting from differences in the liquid junction potentials ($E_{j,ss} - E_{j,s}$) is usually assumed to be within 0.2 pH units for an aqueous soil-solution or dilute soil-suspension given a background electrolyte concentration of approximately 0.01 N (Sposito, 1989).

In these studies, pH of the supernatant and/or the resuspended soil sample

were measured using a Corning Model 130 pH meter and a Fisher Scientific or Orion combination micro-electrode (AgCl saturated 3 M KCl filling solution) following equilibration and analysis of the sample. For suspensions of Webster silty clay loam in methanol/water solutions with a background electrolyte of 0.01 N CaCl_2 , changes in the measured pH (pH_x^{app}) of less than 0.5 pH units were observed going from aqueous to methanol solutions. Recall that a change (δ) of over 2 pH units were previously noted for solutions going from aqueous to methanol solutions. This prompts questions regarding (1) the interactions between the liquid junction potentials arising from the solvent and soil medium; and (2) the effect of methanol on the activity of hydronium ions on the soil surface. Given the difficulty of answering such questions at this time, pH_x^{app} will be used in combination with pK_a' to estimate solute speciation.

Solubility Experiments

Experimental techniques described by Pinal et al. (1990) were employed to measure benzoic acid solubility in methanol/water solutions that were either acidified with 0.01 M HCl or made basic with 0.3 N NaOH. These data were compared to solubilities obtained by Yalkowsky (1985) without additions of an acid or a base. Solute concentrations were analyzed using reversed-phase liquid chromatography (RPLC) techniques. The RPLC system consisted of a ternary solvent pump (LDC Milton Roy Model CM4000, Eldex Model 9600, or Gilson Model 302), a Waters Radial Compression Column with a C-18 cartridge, a UV detector (Gilson Model 115 or Waters Model 490), and a Waters Intelligent Sample Processor (Model 710B or 715). The composition of the mobile phase (acetonitrile/methanol/water; pH2

w/HCl) and the UV wavelength were optimized for analysis of each solute. When necessary, samples were diluted to within an optimal concentration range of the specific analytical method.

Miscible Displacement Experiments

Miscible displacement techniques described by Brusseau et al. (1990) and Lee et al. (1991), were used to estimate retardation factors with water and neat methanol as the eluent for the solutes listed in Table 3-1. The column was packed with air-dried Eustis soil and 0.01 N CaCl_2 solution was pumped through the column until steady-state, water-saturated conditions were established. All solutions were filtered ($0.45 \mu\text{m}$) and degassed with helium before use. The physical properties of the Eustis soil column were as follows: 5 cm length, 0.4 mL/cm^3 volumetric water content (θ), 1.69 g/cm^3 bulk density (ρ), and a column pore volume of 9.64 mL. A pore-water velocity (v) of about 90 cm/hr was used for all experiments.

Solute concentrations in the influent solutions were approximately $100 \mu\text{g/mL}$, except for PCP which was $3 \mu\text{g/mL}$. Solute concentrations in the column effluent were monitored continuously as described by Brusseau et al. (1990) using a flow-through, variable-wavelength UV detector (Gilson Holochrome, Waters 450 or LDC UV) connected to a linear chart recorder (Fisher Recordall 5000). Retardation factors (R) were obtained by calculating the area above the measured breakthrough curves (Nkedi-Kizza et al., 1987). Periodic measurements were made of the column effluent pH with a combination glass electrode using a Corning 130 pH meter or a Brinkman 686 unit.

Equilibrium Sorption Isotherms

Equilibrium sorption isotherms were measured using the batch-equilibration method (Rao et al., 1990). The vials used for this study were 5 mL (1 dram) screw cap borosilicate glass autosampler vials with teflon-lined septa inserts. Amber vials were employed to minimize photolysis. Soil mass to solution volume ratios ranged from 1:2 to 2:3 to achieve sorption of 50% ($\pm 20\%$) of the chemical added. All solutions used had a 0.01 N CaCl_2 matrix unless noted otherwise. Initial solution concentrations added to the soils ranged from 5 to 45 $\mu\text{g/mL}$ for all solutes with the exception of PCP. A concentration range of 0.25 to 3 $\mu\text{g/mL}$ was used in the PCP equilibration studies. All sorption isotherms were measured at room temperature ($T=22\text{--}25^\circ\text{C}$). Following equilibration, the solution and solid phases were separated by centrifuging the soil samples at approximately 300 RCF (relative centrifugal force) using a Sorvall RT6000 centrifuge.

Each isotherm consisted of sorption measured in duplicate at four or more concentrations and at least 30% of the isotherms were replicated. Also for each isotherm, blanks containing the solvent with and without soil were run to check for coelution of any peaks from the soil. Samples were usually equilibrated by rotating for 16-24 hours. For $f_c < 0.2$, degradation was noted after 4 hours in control studies where the soil-solution matrix was removed from the soil and spiked with the appropriate solute concentrations. Therefore, equilibration of samples in solutions of $f_c < 0.2$ was reduced to a maximum of 2 hours with no differences observed in sorption coefficients measured after 1 and 2 hours.

Nonradiolabeled samples were analyzed by RPLC techniques as described previously for the solubility studies. The use of autosampler vials in conjunction with the Waters Intelligent Sample Processor (WISP 715) enabled direct analysis of the samples by RPLC techniques without further sample transfer. The WISP 715 has the capability of varying sampling depths within a vial allowing sampling of the supernatant without removal of the soil. The higher mass to volume ratios (2:3), however, necessitated transfer of the supernatant to a new vial. For ^{14}C -labeled solutes, 0.5 mL aliquots of the supernatant were taken from each sample and mixed with 20 mL of Scinti-Verse II for analysis. Solute concentrations were then assayed using liquid scintillation counting (LSC) methods employing a Searle Delta 300 liquid scintillation counter.

Sorption coefficients, K (mL/g), were estimated by fitting the sorption data to a linear isotherm: $S_e = K C_e$, where S_e and C_e are sorbed ($\mu\text{g/g}$) and solution ($\mu\text{g/mL}$) concentrations, respectively, at equilibrium. The solution concentrations were directly determined, whereas S_e values were determined by difference: $S_e = (C_i - C_e)(V/M)$, where C_i is the initial solution concentration ($\mu\text{g/mL}$) of the solute; V is the solution volume (mL); and M is the soil mass (g).

Results

pK_a Measurements

The pK_a values measured as a function of volume fraction (f_c) methanol increased linearly up to approximately $f_c=0.6$, and then increased markedly at higher cosolvent contents. Representative data for benzoic acid and pentachlorophenol

(PCP) are presented in Figure 3-3. Similar results were observed for the other compounds. For organic bases, a decrease in pK_a' (an acid shift) occurs upon addition of a cosolvent (shift towards neutral species); however, the overall shift from aqueous to neat solvents is usually much less than a single pH unit. Also shown in Figure 3-3 are pK_a' values for benzoic acid determined conductometrically by Pal et al. (1983) up to 80% methanol, and the pK_a' value reported by Bacarella et al. (1955) in neat methanol using a different type of potentiometric method with an electrode system void of a liquid junction. Good agreement between our data and the published data suggests that the procedure used in this study was adequate. The lower pK_a' value obtained in this study for benzoic acid in neat methanol is most likely due to the use of hydrated methanol (0.05%); residual water was removed from the methanol used in the cited studies. Also the constants determined in this study are mixed ionization constants, whereas thermodynamic ionization constants were reported by Bacarella et al. (1955).

Solubility

Solubility data reported by Yalkowsky (1985) for benzoic acid in methanol/water solutions are shown in Figure 3-4. Solubility increased with increasing volume fraction methanol. For the solubility of an organic acid in an unbuffered solution, the pH at saturation will be less than the solute pK_a . For example, the pH of an aqueous solution saturated with benzoic acid is approximately 2.8 (Bates, 1973). Thus, the neutral species dominates over the solubility profile, with over 90% existing in the neutral form at $f_c \geq 0.3$. Also shown in Figure 3-4 are

the solubilities of benzoic acid in acidified methanol/water solutions (0.01 M HCl) measured in this study. At saturation, the acidified samples remained near a pH of 2. Minimal differences were observed between the solubility of benzoic acid in acidified and nonacidified methanol/water solutions. Solubility curves were not measured for other solutes in this study, but benzoic acid is believed to be representative of the general behavior of carboxylic acids in methanol/water solutions. For example, the solubility reported for dicamba in ethanol is over a 100 times greater than its aqueous solubility (Humberg et al., 1989). The observed solubility of benzoic acid in methanol/water solutions is similar to the curve shown in Figure 3-1 for a $\log K_{ow}$ of 2.

To further investigate the effect of speciation on solubility, benzoic acid solubility in solutions containing approximately 0.3 M NaOH was measured for 0 to 40% volume fraction methanol. In the presence of a base, the solubility of benzoic acid was greater than that observed in the unbuffered or acidified solutions. At the solubility limits, the saturated solution pH was 5.0. Given the pK_a ' and measured pH (pH^{app}), speciation of benzoic acid in saturated solutions was estimated to range from approximately 90% to 60% ionized going from aqueous solutions to $f_c=0.4$. The increase observed in solubility with increasing f_c , parallels the increase in the neutral species suggesting that cosolvent effects on benzoate solubility are negligible in the range investigated (i.e., $\alpha_i\sigma_i = 0$).

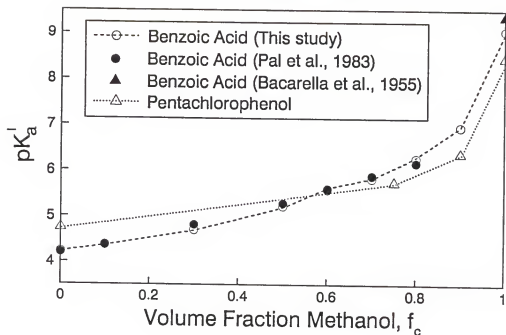


Figure 3-3. Effect of methanol content on the pK'_a of benzoic acid and pentachlorophenol.

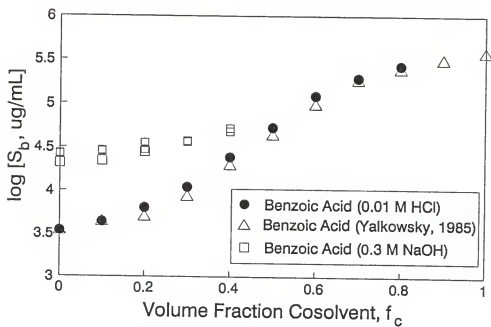


Figure 3-4. Solubility (S_b) of benzoic acid in methanol/water solutions.

Miscible Displacement Studies

The retardation factors (R) estimated from the miscible displacement studies with Eustis soil column are shown in Table 3-2. The column effluent pH ranged between approximately 4 and 4.8 for the different solute/solvent combinations. Comparisons of influent pulse sizes with zero-th moments showed greater than 97% mass recovery for all solute pulses. Loss of soil organic matter from the soil column during elution with methanol was considered negligible as shown previously by Lee et al. (1991). For the substituted phenols, R values determined in methanol were smaller than those water ($f_c=0$). For both chlorophenols in neat methanol, retardation factors decreased to one corresponding to no sorption ($R=1$). A decrease in R with increasing f_c is expected from the log-linear cosolvency model in the absence of any specific interactions. The opposite trend, however, was observed for all of the substituted benzoic acids. Benzoic acid and dicamba were chosen for further investigation in several methanol/water solutions using batch techniques with PCP included as a control. For the batch studies, Webster soil with a higher organic carbon content was used to better differentiate sorption in the various methanol/water solutions. Although the greatest increase in retardation was observed with gentisic acid, preliminary batch isotherm data exhibited extreme nonlinearity (data not shown). Since problems associated with isotherm nonlinearity may confound assessment of the proposed model, further investigation of gentisic acid was not pursued.

Table 3-2. Retardation factors for several organic acids in aqueous and methanol solutions from Eustis Soil.

Solute	Retardation Factors	
	Aqueous	Methanol
<u>Substituted Phenols</u>		
Pentachlorophenol	4.7	1.0
2,4-Dichlorophenol	3.6	1.0
Picric Acid (2,4,6-trinitrophenol)	1.9	1.4
<u>Substituted Benzoic Acids</u>		
Gentisic Acid (2,5-dihydroxy acetic acid)	1.9	3.1
2,4,5-Trichlorophenoxy Acetic Acid	1.7	2.1
2,4-Dichlorophenoxy Acetic Acid	1.4	2.7
Benzoic Acid	1.2	2.2
Pentafluorobenzoic Acid	1.0	1.6
Dicamba	1.0	2.0

Batch Equilibration Studies

Sorption of benzoic acid, dicamba, and PCP by Webster soil was measured from several methanol/water solutions. Representative isotherms are shown in Figure 3-5. Sorption isotherms were linear for PCP and dicamba in both aqueous and mixed-solvent systems over the concentration range investigated. Sorption isotherms for benzoic acid were slightly nonlinear, but a linear approximation of the sorption coefficients (K) adequately described the data. The correlation coefficients (r^2) ranged between 0.95 and 1.0.

Effect of Solvent Addition

As noted previously, addition of an organic cosolvent to an aqueous solution results in an increase in the pK_a' for organic acids. Changes in speciation become significant at $f_c > 0.5$ as marked changes occur in the pK_a' values. In neat methanol, the measured soil-solution pH for Webster soil ranged between 6.2 and 6.5; therefore, essentially all the benzoic acid and PCP existed in the neutral form, while 20% to 30% of dicamba remained ionized.

The sorption coefficients estimated from batch equilibration studies of PCP and benzoic acid are plotted in Figure 3-6 as a function of volume fraction methanol (f_c). Sorption of PCP in methanol/water systems was well described by the log-linear model with speciation given by Eq. (3-6) (Figure 3-6A) except in neat methanol. Of the required model parameters, bulk pH and pK_a' were measured; ϕ_n was estimated using Eq. (3-5); and $K_{w,i}$, $K_{w,n}$, $\alpha_i\sigma_i$, and $\alpha_n\sigma_n$ were taken from Lee et al. (1990) where sorption of PCP was measured as a function of f_c while pH was maintained such that

PCP was either completely ionized or completely neutral. The values for $K_{w,i}$ and $K_{w,n}$ were adjusted for differences in the OC content of the Webster soil used in the two studies (i.e., $K = K_{oc} \text{ OC}$).

Benzoic acid sorption decreased with the addition of methanol up to $f_c \leq 0.2$, but then increased with f_c thereafter (Figure 3-6B). Eq. (3-6) was applied to the benzoic acid data using four reasonable parameter sets to investigate if this behavior was mostly due to changes in speciation with methanol additions. For all cases, the sorption coefficient for benzoate ($K_{w,i}$) was measured at $\text{pH} = 6.9$; $K_{n,w}$ was estimated by measuring the K_w at $\text{pH} = 3.0$ and applying Eq. (3-4); and σ_n was estimated by regressing benzoic acid solubility data in methanol/water solutions (data in $f_c = 0$ to 0.8 ; Yalkowsky, 1985). Two values for σ_i were used. In one case, σ_i was set equal to zero as suggested by the solubility data (Figure 3-4), and in the second case, σ_i was set equal to 0.65 as estimated from the initial portion of the $\log K_m$ versus f_c curve (i.e., $f_c \leq 0.2$) where benzoic acid remained $\geq 99\%$ ionized. For two parameter sets, solvent-sorbent interactions were ignored ($\alpha_n = \alpha_i = 1$) while in the remaining two parameter sets an average α value of 0.5 observed by Fu and Luthy (1986b) for several solute, soil, and solvent combinations was used as an initial estimate of solvent-sorbent interactions. In all cases, Eq. (3-6) failed to adequately predict the magnitude of sorption observed for benzoic acid at higher methanol contents (Figure 3-6B). Similar sorption data were observed for dicamba (data not shown). Model parameters were estimated for the dicamba sorption data in a manner analogous to the calculations for benzoic acid with similar results.

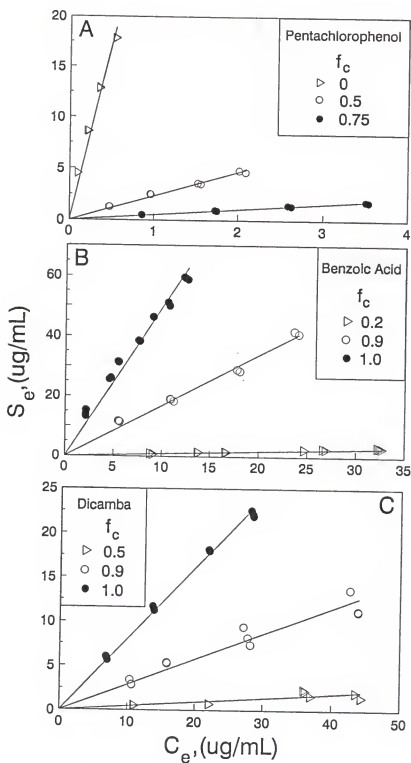


Figure 3-5. Representative sorption isotherms for (A) pentachlorophenol, (B) benzoic acid, and (C) dicamba, on Webster soil in various methanol/water solutions.

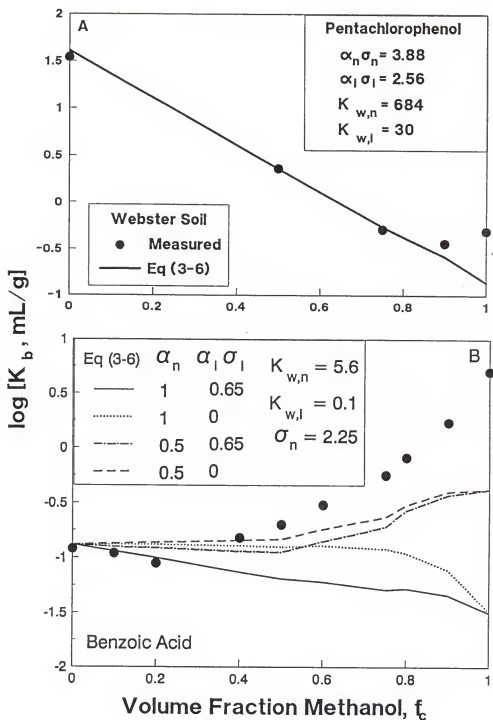


Figure 3-6. Measured and predicted sorption by Webster soil of (A) pentachlorophenol, and (B) benzoic acid as a function of volume fraction methanol (f_v).

Discussion

Cosolvent effects on solubility and sorption of nonpolar organic solutes can be readily predicted using the log-linear model, and most deviations from this model can be explained by invoking water-cosolvent interactions (Pinal et al., 1991). In contrast, prediction of sorption of ionizable organic solutes from mixed solvents is confounded by a number of indirect effects resulting from cosolvent-induced phenomenon occurring either in the solution phase or on the sorbent. The presence of the neutral species of an ionizable organic solute is increasingly favored with increasing cosolvent content (alkaline shift in the pK_a'), such that in a neat cosolvent the amount of the ionized species present may be negligible. The cosolvency model given by Eq. (3-6) accounts for such changes in speciation, but underestimated the magnitude of carboxylic acid sorption from methanol-water; this suggests the significance of other mechanisms.

Solute-solvent Interactions

Solution-phase interactions not considered in formulating Eq. (3-6) include cosolvent-enhanced polymerization and ion-pairing. Polymerization of benzoic acid in neat methanol could not be measured up to a concentration of 10 mg/mL.; therefore, enhanced sorption arising from the former mechanism was discounted. The formation of ion-pairs may be promoted by the addition of an organic cosolvent to an aqueous solution resulting from a decrease in the dielectric constant of the solution (Swarc, 1974); increase in pK_a' with f_c is directly related to decreasing dielectric constant. Even though the neutral form of the carboxylic acid is the

predominant species at higher cosolvent fractions, hydrogen from the neutral acid may be displaced by the cations in the electrolyte matrix (e.g., 0.01 N CaCl_2 in the present study). Solvent-enhanced ion-pairing could result in the formation of either neutral or charged ion-pairs in solution. Since neutral ion-pairs have been shown to behave in a manner similar to nonpolar organic compounds (Lee et al., 1990; Westall et al., 1985), their sorption should only decrease with increasing cosolvent content. However, the formation of positively charged ion-pairs followed by exchange on negatively charged soil surfaces would result in an increase in sorption.

To assess the role of the formation of charged ion-pairs (e.g., Ca-carboxylate^+), benzoic acid sorption was measured by K^+ -saturated Webster soil and compared with measurements from where Ca^{+2} dominated the Webster soil CEC sites, and the effect of CaCl_2 concentration on benzoic acid sorption was investigated. Sorption of benzoic acid by a K^+ -saturated Webster soil did not exhibit the same behavior as observed earlier with the Ca^{+2} dominated soil (Figure 3-6B) where sorption increased upon methanol addition. Note that this experiment was done on a more recently obtained subsample of Webster soil (see Chapter 5). The sorption coefficients measured for benzoic acid on the K^+ -saturated soil were 0.4 mL/g and 0.1 mL/g for $f_c=0.26$ and 0.66, respectively, compared to 0.3 mL/g and 0.7 mL/g obtained from the Ca^{+2} -saturated sample. This demonstrates the significance of electrolyte composition on the sorption of HIOCs and the possibility of cosolvent-induced formation of positively charged ion-pairs. From this conclusion an increase in sorption with increasing Ca^{++} concentrations would be expected; however, no

significant changes were observed in the sorption of benzoic acid with increasing CaCl_2 concentrations (0.002 to 0.05 N) from either a 25% methanol solution or neat methanol. This apparent contradiction indicates the presence of a different sorption mechanism that is similarly impacted by cation-type. For example, an increase in valence state of a cation, i.e., K^+ versus Ca^{++} , enhances polarization of the molecules in the solvation sphere of the cation and results in stronger hydrogen bonding characteristics (Bailey et al., 1968). This mechanism may be of particular importance for methanol considering the pronounced hydrogen-bonding characteristics of alcohols. Also, cation-type affects the probability of cation- versus water-bridging (i.e., inner- versus outer-sphere complexation) as previously discussed in Chapter 1. To further elucidate the processes of importance, a preliminary assessment of the sorption of benzoic acid on other sorbents from aqueous and methanol solutions will be made in the Chapter 4.

Desorption Characteristics

A preliminary desorption experiment was performed to assess the reversibility of the sorption mechanism and the potential for chemisorption. An adsorption isotherm was measured in triplicate for a single concentration of benzoic acid (40 $\mu\text{g/mL}$) at a mass to volume ratio of 2 using a subsample of Webster soil and 0.01 N CaCl_2 methanol. (Note this Webster subsample was taken from the Webster site in Iowa a year after the batch that was used in the previous experiments.) After equilibration, centrifugation, and sampling for analysis, the remaining methanol was decanted and replaced with an aqueous 0.01 N CaCl_2 solution (resulting f_c was

approximately 0.22) and reequilibrated for 16 hours. The single point sorption coefficients for the adsorption from neat methanol and the desorption from $f_c \approx 0.22$ was 12 mL/g and 0.4 mL/g, respectively. These data suggest that the sorption process is reversible and hysteresis minimal.

Estimation of pH by pH^{app}

A brief discussion on the impact of assuming that pH^{app} was a reasonable estimate of the soil-solution pH relative to assessing observed deviations from Eq. (3-6) is now warranted. If the true pH of the soil-solution was higher than pH^{app} as was observed in the absence of soil, predictions from Eq. (3-6) would be similar to that observed for parameter set #2 in Figure 3-2. This prediction would still underestimate the overall sorption observed. Alternately, if surface acidity increased with increasing cosolvent addition (i.e., pH at the surface decreases with f_c , thus $\text{pH} - \text{pK}_{a,w}$ becomes increasingly more negative), increased sorption may occur. However, as previously discussed, Loeppert et al. (1979) observed no apparent change in surface acidity of montmorillonite (the dominate clay in Webster soil) in neat methanol. Also, similar suppositions did not need to be invoked to describe the data for chlorophenols. Problems associated with using inaccurate pH estimates in Eq. (3-6), however, cannot be completely ruled out especially given the difficulty in assessing the differences between the true soil-solution pH and pH^{app} in mixed solvents.

An added level of complexity arises when an attempt is made to define what the pH is that is directly influencing solute speciation at the soil surface (e.g., *effective* pH), thus sorption. For the case of soil and inorganics, it has been proposed that the

distribution of cations on the soil surface and in the diffuse double layer gives rise to the potential of an *effective* pH (e.g., pH at the soil surface) much lower than that measured in the bulk solution. In measuring the distribution of various dyes between an immiscible organic liquid and an aqueous solution (liquid-liquid equilibria), a similar decrease in pH at the liquid-liquid interface was noted for amine-type dyes (Peters, 1931). However, dyes containing long chain carboxylic acid groups resulted in a pH at the liquid-liquid interface much greater than the pH measured in the aqueous solution (≈ 2 pH units) (Peters, 1931). An alkaline shift in the sorption versus pH curve observed for the sorption of 2,4-dichlorophenoxy acetic acid by soils (Nicholls and Evans, 1991) also implies an *effective* pH at the surface less than that measured in the bulk. Lee et al. (1990) found that the sorption of PCP from aqueous solutions by soils could be adequately described by using the measured soil-solution pH and the solute pK_a to estimate solute speciation. Similar success was shown in Chapter 1 for the sorption of several organic acids by soil (Figure 1-2 and 1-3). The apparent contradiction between measured pH and *effective* pH for the different solutes suggests that either a misinterpretation of the macroscopic response observed or that the *probing* solute locally alters the surface pH upon interaction.

Summary

Sorption of substituted chlorophenols and carboxylic acids by soils was measured from methanol-water solutions. Decreased sorption in methanol compared to that measured in aqueous solutions was observed for the substituted phenols investigated; this trend is similar to that observed for nonpolar organic solutes.

Sorption of PCP was adequately characterized by combining the log-linear cosolvency model for predicting cosolvency effects with the model demonstrated by Lee et al. (1990) for describing speciation effects. For carboxylic acids, the magnitude of sorption observed in methanol/water solutions could not be predicted. Inclusion of cosolvent-induced changes in pK_a' and the uncertainty of the formation and exchange of charged ion-pairs suggest that deviations from Eq. (3-6) predictions may be due to other types of solvent-driven complexation reactions (e.g., hydrogen bonding, cation- and water-bridging). Inaccurate assessments of the observed deviations from Eq. (3-6) due to the potential errors associated with measuring soil-solution pH in mixed solvents should also not be excluded.

Further research is needed to better understand the influence of ionic equilibria on the sorption of organic acids in solvent/water solutions. This warranted an investigation of the impact of pH within a given solvent/water fraction on the sorption of benzoic acid by Webster soil. In addition, the apparent contradiction between the insignificant impact of increasing CaCl_2 concentrations on benzoic acid sorption versus the differences observed between Ca^{++} - and K^+ saturated Webster soil warrants a preliminary assessment of benzoic acid sorption by various sorbents from aqueous and methanol solutions. Both the impact of ionic equilibria and elucidation of the sorption process will be presented in the next chapter.

CHAPTER 4

IMPACT OF pH ON SORPTION OF BENZOIC ACID FROM METHANOL/WATER SOLUTIONS

Introduction

Separation and analysis of hydrophobic ionizable organic compounds (HIOCs) using liquid chromatography has been carried out almost exclusively by ion-exchange columns (Jandera and Churacek, 1973; Horvath, 1973). As the use of reversed-phase chromatographic (RPLC) supports increased exponentially, investigations on the utility of RPLC supports in separation of HIOCs were initiated (Horvath et al., 1976). In RPLC, the distribution of a compound is between a nonpolar stationary phase (i.e., alkyl chains or rings chemically bonded to a silica gel support) and a polar mobile phase composed of water plus organic modifiers (e.g., methanol or acetonitrile). Consensus on the retention mechanism of hydrophobic organic compounds (HOCs) by RPLC supports is that solute-solvent interactions dominate (Horvath et al., 1976, 1977). However, the influence of ionic equilibria on HIOCs behavior warranted investigations on the impact of pH on retention of HIOCs in RPLC. With increasing volume fraction cosolvent (f_c) and pH (buffered within 3 and 7), decreasing retention by RPLC supports has been reported for carboxylic acids

from methanol/water solutions ($f_c \leq 0.5$) (Marques and Schoenmakers, 1992; Schoenmakers et al., 1991; Van De Venne et al., 1978), and for chlorophenols from acetonitrile/water solutions ($f_c \leq 0.6$) within the same pH range (Bourguignon et al., 1993). Models similar to that presented in Chapter 3 (Eq. 3-6) for sorption of organic acids by soils in mixed solvents have been employed to successfully describe retention of organic acids in RPLC. Shown in Figure 4-1 are RPLC retention data and model predictions (Schoenmakers et al., 1991) for benzoic acid as a function of pH and methanol composition using mobile phases buffered with 1:2 stoichiometric mixtures of citrate and phosphate with sodium as the counter ion. Model predictions by Schoenmakers et al. (1991) were derived in a manner analogous to that given in Chapter 3 (Eq. 3-6). The chromatographic retention model presented by Schoenmakers et al. (1991) is defined in terms of chromatographic capacity factors, whereas, the sorption model presented in Chapter 3 uses sorption coefficients.

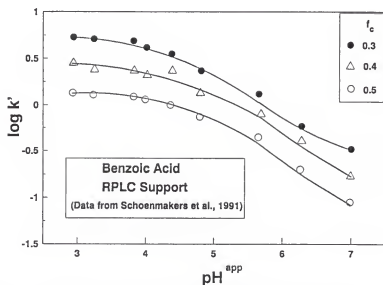


Figure 4-1. Retention data for benzoic acid as a function of pH^{app} at different methanol fraction (v/v) by RPLC.

The impact of speciation changes, resulting from cosolvent-induced changes in the solute pK_a' , on organic acid sorption was explored in the Chapter 3. For carboxylic acids, the magnitude of sorption observed in methanol/water solutions could not be predicted by combining the log-linear cosolvency model which was successful for describing sorption of HOCs from mixed solvents, and a speciation model successfully used to describe sorption of HIOCs from aqueous solutions (Eq. 3-6). Inclusion of cosolvent-induced changes in pK_a' and elimination of the charged ion-pair formation in solution suggested that observed deviations from Eq. (3-6) predictions were probably due to specific, surface complexation reactions. Consideration was given to the potential errors associated with measuring soil-solution pH in mixed solvents and how these errors might effect model predictions; however, this issue was not definitively resolved.

An investigation of the impact of pH changes within a given solvent/water fraction may help to better differentiate the roles of the ionized and neutral species on the overall sorption of carboxylic acids by soils. An estimate of pH will be done as in Chapter 3 by using the measured pH of the soil solution (pH^{app}) without any corrections. Schoenmakers et al. (1991) also used pH^{app} as an estimate of the system pH (Figure 4-1). Note that comparing pH effects at a given volume fraction cosolvent (f_c) is less problematic than comparing cosolvent effects at a given pH, especially at high f_c (i.e., the trends within a given solvent/water solution will be similar). Therefore, an investigation of pH effects at a given f_c on sorption of organic acids may also help to elucidate the *effective* pH of the soil-suspension in mixed solvents.

In this study, sorption of organic acids was measured as a function of pH at several methanol fractions with the most attention given to data collection of benzoic acid sorption by Webster soil. However, to further elucidate the mechanisms of importance for benzoic acid sorption by soils and how to relate various solute and sorbent characteristics to the sorption process, preliminary data was collected for benzoic acid sorption by other sorbents in aqueous and neat methanol solutions as well as for sorption of PCP by Webster soil in methanol/water solutions.

Materials and Methods

Sorbents

The sorbent used in this study was a Webster silty clay loam (Typic Haplaquoll) from Iowa containing 30.7% sand, 42.8% silt, 27% clay, and 3.0% organic carbon (OC). Soil samples were air-dried and passed through a 2 mm sieve prior to use. For the equilibration studies conducted at different pHs (range 3 to 9) subsamples of the Webster soil were further treated to be homoionic with Ca^{2+} using a method similar to that employed by Rhue and Reeve (1990). Soil (25 grams) was equilibrated in 250-mL polycarbonate centrifuge bottles with 125 mL of 1.0 N calcium acetate adjusted to the desired pH with either hydrochloric acid (HCl) or sodium hydroxide (NaOH), centrifuged and decanted. This procedure was repeated twice, followed by two washes with pH adjusted 1.0 N CaCl_2 . Final rinsing with ethanol was done to remove excess salts. The presence of excess salts was tested by adding a few drops of silver nitrate to the supernatant. Ethanol rinsing continued until no precipitate (AgCl) was detected in the supernatant. The soils were then air-dried, gently ground, and stored for future use.

Analysis of OC content, cation exchange capacity (CEC), and total elemental analysis were performed on the treated soils to assess the effect of the pH treatments. No change was observed in the OC content of the soil before and after pH treatment, as determined using the Walkley-Black method (Nelson and Sommers, 1988). The cation exchange capacity (CEC) was measured on the pH-treated soils using a procedure denoted as "method II" by Rhue and Reve (1990). The pH of the solutions during extraction for determining CEC was similar to the pH of the treated soils. Elemental analysis was performed by a laboratory in the Soil and Environmental Department at UC-Riverside using a technique by Bakhtar et al. (1989). This method involved digesting 0.5 g soil samples with a peroxide/acid solutions followed by elemental analysis by inductively coupled optical emission and absorption spectrometry. Solutions from sample digests were diluted 500 fold for all elemental analysis with the exception of Si which required a 50,000 fold dilution. Results from the elemental analysis and CEC are given in Table 4-1.

Chemicals

Pentachlorophenol (PCP) and benzoic acid were used in this study (Chemical characteristics are given in Table 4-2). The crystalline compounds were all of >98% purity. Of the solvents employed, methanol (high purity, HPLC grade) was purchased from J.T. Baker and used without further preparation, and the water was deionized. Uniformly ring-labeled [^{14}C] pentachlorophenol (PCP) and benzoic acid (specific activity, 12 mCi/mmol and 13.3 mCi/mmol, respectively) was purchased from Pathfinders Laboratories with a radiopurity of 99.6%, and a chemical purity of >98%.

Table 4-1. Cation exchange capacity (CEC) in cmol(+)/kg and elemental analysis in mg/kg of pH treated Webster soils.

Element	pH Treatment				
	3	4	5	9	Untreated (7)
CEC	30	42	35	42	40
Ca	7,050	9,250	10,200	10,300	9,080
Mg	3,870	4,380	4,690	4,140	4,850
Na	7,090	6,910	6,770	8,130	7,490
K	11,200	14,000	14,000	12,500	13,600
P	383	415	502	420	434
Si	288,000	292,000	279,000	283,000	267,000
B	24.3	30.5	24.5	24.1	19
Ba	434	482	541	495	420
Sr	113	116	126	131	111
Li	11.1	15	14	11.4	12
Ti	2,250	2,440	2,530	2,280	2,090
Al	47,000	49,500	52,300	47,400	45,000
Fe	22,700	24,600	26,200	21,200	21,900
Mn	322	387	503	362	376
Cu	2.14	12.1	32.2	19.1	ND
Zn	53.3	61.1	66.1	52.7	45
V	52.1	68	68.6	53.6	62.5
Ni	15.1	18.1	18.5	14.2	14
Co	3.11	5.22	4.69	3.17	6.32
Cr	33.3	41.3	45.2	31.8	37.1
Be	2.38	2.82	2.89	2.48	1.67
Ba	24.1	44.7	35.1	14.1	32.7
Y	11.5	13.6	14.1	11.5	10.5
Total	12,100	13,900	14,800	13,800	11,700

Table 4-2. Chemical characteristics of benzoic acid and pentachlorophenol (PCP).

Solute	MW ^a (g/mole)	log K _{ow,n}	Solubility		pK _a ^c	
			Water	Methanol	Water	Methanol
PCP	266.4	5.01	14 ^a	VS ^c	4.74	8.45
Benzoic Acid	122.1	1.87	3,000 ^b	360,000 ^b	4.22	8.96

^a Verschuren (1983); ^b Yalkowsky EPA report; ^c Very Soluble (Dean, 1985);
^d Measured.

Equilibrium Sorption Isotherms

Equilibrium sorption isotherms were measured using the batch-equilibration method (Rao et al., 1990). The vials used for this study were 5-mL (1 dram) screw cap borosilicate glass autosampler vials with teflon-lined septa inserts. Amber vials were employed to minimize photolysis. Mass to volume ratios ranged from 2:3 to 1:2 to achieve sorption of about 50% of the chemical added. All methanol/water solutions used had a 0.01 N CaCl₂ matrix. Initial solution concentrations applied to the soils in the equilibration studies ranged from 5 to 45 µg/mL and 0.25 to 3 µg/mL for benzoic acid and PCP, respectively. All sorption isotherms were measured at room temperature (22 ± 2 °C). Following equilibration, the solution and solid phases were separated by centrifuging the soil samples at approximately 300 RCF (relative

centrifugal force) using a Sorvall RT6000 centrifuge. After analysis, pH measurements of the supernatant and/or the resuspended sample were made using a Corning Model 130 or a Fisher Accumet Model 925 pH meter and an Ingold micro-electrode (AgCl saturated 3 M KCl filling solution).

Sorption isotherms consisted of data collected in duplicate at no fewer than three concentrations. Most isotherm experiments were also repeated. Blanks containing the solution matrix with and without soil were run along with the samples to check for coelution of any peaks from the soil in the HPLC analysis or to obtain an appropriate background count in the LSC analysis. In the case of the soil treated to $\text{pH} \approx 8$, an unidentified peak eluted at the same retention time as benzoic acid; therefore, the area response from this peak was subtracted from the known sample peak. Samples were usually equilibrated by rotating for 16-24 hours. In control studies where solutions decanted from a pre-equilibration of uncontaminated soil with 20% methanol were spiked with appropriate solute concentrations, degradation of benzoic acid was noted after 4 hours. Therefore, samples in solutions of $f_c < 0.2$ were equilibrated for a maximum of 2 hours; no differences were observed between sorption coefficients measured after one and two hours of equilibration time.

Solute concentrations of nonradiolabeled samples and radiolabeled samples were analyzed using previously described (Chapter 3) reversed-phase liquid chromatography (RPLC) and liquid scintillation counting (LSC) techniques, respectively, and sorption coefficients (K , mL/g) were estimated by difference from initial and equilibrium solute concentration data (Chapter 3).

Results and Discussion

Sorption of benzoic acid and PCP by Webster soil adjusted to different pH values was measured from several methanol/water solutions. In the concentration range investigated, PCP sorption isotherms were linear in both aqueous and mixed-solvent systems. For benzoic acid, sorption isotherms were slightly nonlinear; however, a linear approximation of the sorption coefficients (K) was still considered adequate. Representative isotherms for sorption of benzoic acid are shown in Figure 2. Correlation coefficients (r^2) were greater than 0.92 for most data sets with smaller r^2 values usually resulting from a scatter in the data rather than from nonlinear behavior. For completeness, the coefficients from a Freundlich fit to the benzoic acid isotherm data are shown in Table 4-3 along with a linear approximation of the sorption coefficients.

Table 4-3. Parameters for linear and Freundlich fits to the isotherm data for benzoic acid as a function of pH and f_c .

f_c	pH	$K_d(\text{mL/g})$	$K_f(\text{mL}^N \mu\text{g}^{1-N} \text{g}^{-1})$	$N \pm \text{SE}$
0	3.63	4.84	7.69	0.75 ± 0.02
	3.68	4.32	7.80	0.72 ± 0.04
	4.9	1.15	2.28	0.75 ± 0.02
	4.81	1.0	2.45	0.70 ± 0.04
	6.9	0.12	0.07	1.10 ± 0.06
	8.2	0.06	0.07	0.92 ± 0.10
0.10	3.59	3.38	5.17	0.78 ± 0.02
	3.75	2.26	3.78	0.78 ± 0.01
	4.85	0.80	1.57	0.77 ± 0.04
	5.3	0.54	0.96	0.81 ± 0.03

(Table 4-3 continued)

f_c	pH	$K_d(\text{mL/g})$	$K_f(\text{mL}^N \mu\text{g}^{1-N} \text{g}^{-1})$	$N \pm \text{SE}$
0.10	6.9	0.11	0.13	0.89 ± 0.21
	8.4	0.098	0.07	1.13 ± 0.28
0.50	3.9	0.55		
	5.4	0.30		
	5.62	0.28	0.14	1.21 ± 0.02
	6.9	0.20	0.12	1.16 ± 0.05
	7.9	0.24	0.17	1.13 ± 0.11
0.75	4.0	0.22		
	5.12	0.50	0.30	1.15 ± 0.08
	5.5	0.47	0.57	0.93 ± 0.04
	5.8	0.71		
	6.15	0.67	1.0	0.86 ± 0.04
	6.2	0.66		
	6.7	0.63		
	6.8	0.56	0.37	1.16 ± 0.05
	6.83	0.53		
	6.9	0.50	0.31	1.15 ± 0.04
	7.2	0.57	0.84	0.87 ± 0.07
	7.9	0.54		
	8.2	0.45	0.26	1.16 ± 0.18
0.8	4.78	0.32	0.54	0.84 ± 0.06
	5.3	0.59	0.51	1.0 ± 0.18
	6.6	0.81	1.32	0.85 ± 0.02
	7.8	0.55	0.25	1.26 ± 0.05
	6.6	1.088	0.78	1.13 ± 0.24
	5.45	0.58	0.81	0.80 ± 0.05
	6.2	0.82	0.77	1.10 ± 0.10
	7.1	0.78	0.96	0.93 ± 0.02
	8.3	0.67	0.77	0.95 ± 0.04
0.9	3.6	.31	.5	0.79 ± 0.05
	3.9	0.46		
	4.75	0.85	1.81	0.74 ± 0.04
	5.13	1.05		
	5.3	1.23	2.76	0.70 ± 0.05
	5.8	1.52		
	6.58	1.86	2.21	0.94 ± 0.02
	6.7	1.70	2.50	0.86 ± 0.03
	7.8	1.45		

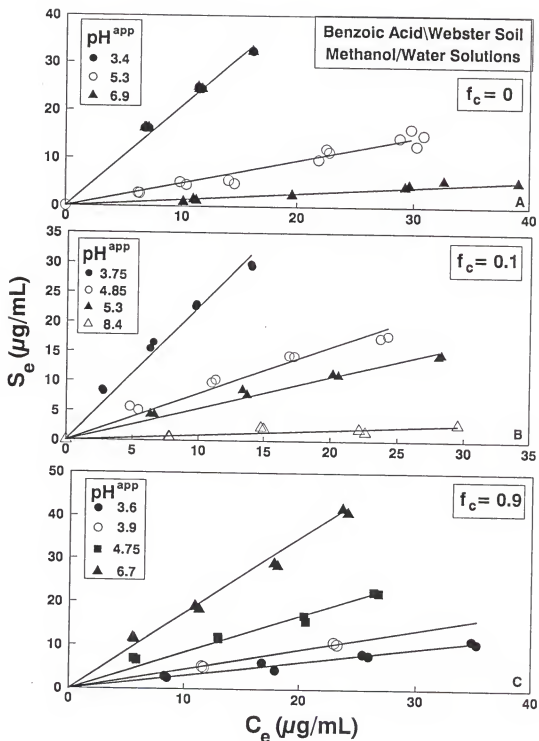


Figure 4-2. Representative isotherms for benzoic acid in (A) aqueous solutions; (B) $f_c=0.1$; and (C) $f_c=0.9$ buffered at several pH values.

Effects of pH on Benzoic Acid Sorption at $f_c \leq 0.5$

Sorption coefficients estimated from batch equilibration studies of benzoic acid in methanol/water solutions ($f_c \leq 0.5$) are plotted as a function of pH^{app} in Figure 4-3. Also included in Figure 4-3 are predictions based on an equation analogous to Eq. (3-4):

$$K_b = K_{b,n} \phi_{b,n} + K_{b,i} (1 - \phi_{b,n}) \quad (4-1)$$

where $K_{b,n}$ and $K_{b,i}$ are the sorption coefficients in the binary solvent solution of interest of the neutral and ionized species, respectively. Recall that the conditional dissociation constant (pK_a') increases with increasing methanol content; therefore, the fraction of the species that is neutral ($\phi_{b,n}$) is based on the pK_a' determined in the solvent mixture. Values for $K_{b,n}$ and $K_{b,i}$ were estimated from the measured sorption data at the lowest and the highest pH^{app} , respectively. The patterns of decreased sorption observed with increasing pH^{app} , and the decrease in $K_{b,n}$ values with increasing f_c resemble the curves shown in Figure 4-1 for retention of benzoic acid in RPLC. However, at the higher pH values where benzoate dominates, sorption by soils increased while retention by RPLC supports continued to decrease. Note, however, that for the RPLC data exemplified in Figure 4-1 mobile phases were buffered with 1:1 stoichiometric mixtures of citrate and phosphate with sodium as the counter ion. Recall from Chapter 3 that the use K^+ -saturated Webster soil resulted in the opposite sorption trends with f_c compared to the Ca^{+2} -saturated Webster soil. Therefore, the differences observed between the soil and RPLC data could very well be due to the different electrolyte composition.

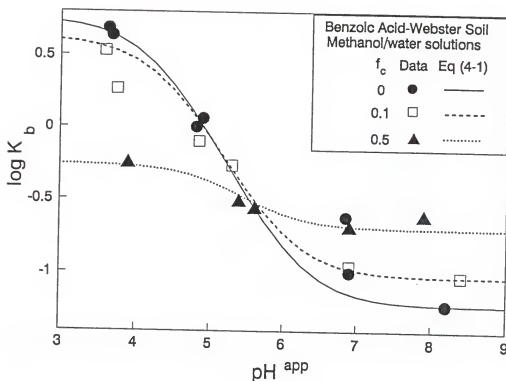


Figure 4-3. Sorption of benzoic acid by Webster soil buffered at different pH^{app} values in methanol/water solutions of $f_c \leq 0.5$.

Effects of pH^{app} on Benzoic Acid Sorption at $f_c \geq 0.75$

To further investigate the effect of pH and solvent composition, sorption of benzoic acid was measured at higher methanol volume fractions ($f_c \geq 0.75$). The $\log K_b$ values estimated from these studies are plotted as a function of $\text{pH} - \text{pK}_a'$ in Figure 4-4. At higher methanol fractions, the curves are the inverse of those observed at $f_c \leq 0.05$ (Figure 4-3); the magnitude of sorption and $\log (K_{b,n}/K_{b,i})$ now increases with pH and f_c , respectively. Also note that sorption appears to be at a maximum where $\text{pH} = \text{pK}_a'$. Anion exclusion at relatively high pH values has been noted for RPLC supports (Schoemakers et al., 1991) where the solute and the unreacted silanol

groups on the sorbent become increasingly more negative. Soil surfaces, unlike RPLC supports, are predominately negatively charged over a large pH range. Exclusion of inorganic anions by soils with high clay contents has been observed in aqueous systems; however, a similar phenomenon was not observed for benzoic acid in aqueous and low f_c solutions.

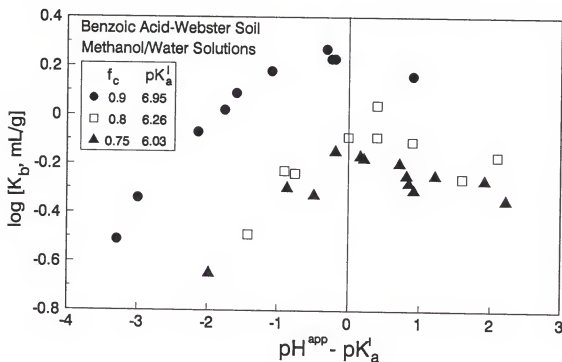


Figure 4-4. Sorption of benzoic acid by Webster soil buffered at different pH values in methanol/water solutions of $f_c=0.75, 0.8$, and 0.9 .

Effects of pH^{app} on PCP Sorption at $f_c \geq 0.75$

To investigate whether this phenomenon with benzoic acid was an anomaly, PCP sorption by Webster soil was also measured as a function of pH in $f_c = 0.75$ and in neat methanol. At $f_c=0.75$, PCP sorption decreased with increasing pH, similar

to that observed in aqueous solutions, and was well described by Eq. (4-1) (Figure 4-6). In neat methanol, however, PCP sorption increased with increasing pH (Figure 4-6) similar to that observed for benzoic acid at $f_c \geq 0.75$. The cosolvency curve for PCP in neat methanol also begins to decrease at a higher pH ($\text{pH}^{\text{app}} > 6$) similar to that observed for benzoic acid in high methanol fractions. The decrease, however, begins at pH^{app} much smaller than the pK_a' of PCP (8.45) in neat methanol. Comparisons of $(\text{pH}^{\text{app}} - \text{pK}_a')$ and the pK_a' values given in Figure 4-5, shows that the initial decrease in sorption of benzoic acid at high f_c values also begins at $\text{pH}^{\text{app}} > 6$. This phenomenon does not appear to happen in aqueous solutions or at lower methanol contents; therefore, it can only be attributed to solvent-sorbent interactions.

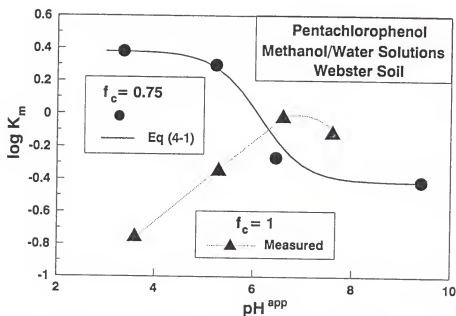


Figure 4-5. Sorption of PCP by Webster soil buffered at different pH values in methanol/water solutions of $f_c = 0.75$ and 1.0.

In reversed-phase liquid chromatography (RPLC), high ionic strength buffers (≥ 0.05 M) are used to adjust the pH of the mobile phase, thus limiting the amount

of organic modifier that may be used. Problems with buffer precipitation begin to occur at about 75% volume fraction of organic modifiers (i.e., methanol, acetonitrile) typically used in RPLC. However, sorption studies presented here were conducted with soils prepared at different pH values such that buffers were not needed to achieve various pH values. Also the ionic strength of the solutions employed was maintained at 0.01 N with CaCl_2 which is much less than the ionic strengths of the solutions typically used in RPLC. However, to verify that the observed sorptive behavior was not due to a precipitation reaction, radiolabelled benzoic acid experiments analogous to those described for soils were conducted using 250 μM glass beads in $f_c=0.9$ solutions in the 3 to 9 pH range. No measurable sorption by the glass beads was observed, suggesting that artifacts due to precipitation were not present.

Sorption of Neutral Benzoic Acid Relative to Benzoate

From the sorption data obtained as a function of pH and methanol content, separate cosolvency curves can be characterized for neutral benzoic acid and benzoate. Sorption coefficients for neutral benzoic acid and benzoate at various methanol contents were obtained from the sorption experiments where pH^{app} was at least one pH unit below or above the pK_a' . The compiled data are shown in Figure 4-6A along with slopes and lines estimated from regressing $\log K_b$ and f_c data for neutral benzoic acid ($0 \leq f_c \leq 0.75$) and benzoate ($0 \leq f_c \leq 0.8$), respectively. (Note the K_b at $f_c=1$ was obtained from Figure 3-6; $[\text{pH}^{\text{app}} - \text{pK}_a'] > 2$). Also shown in Figure 4-6 is a similar plot for the benzoic acid retention data by RPLC supports.

Unlike the sorption data obtained for neutral and ionized PCP in methanol/water

solutions by Lee et al. (1991), where sorption for both species decreased with increasing f_c , and the RPLC data shown in Figure 4-6B, benzoate sorption increased with methanol content. Based on the almost one to one inverse correlation between the slopes from regression of neutral benzoic acid and benzoate data, and assuming the individual processes were additive, sorption would be expected to be approximately constant over the f_c range regressed. If the slopes were exactly proportional, then the two lines would intersect at $f_c=0.5$; however, slight differences in the absolute values of the two slopes yields an intersection at f_c of approximately 0.6.

From the slope of the neutral benzoic acid methanol/water sorption data ($\alpha_n \sigma_n = 1.32$) and the σ_n value of 2.25 for benzoic acid methanol/water solubility data (Yalkowsky, 1985), α_n equals 0.8 which is midway between the two of the Eq. (3-6) predictions given in Figure 3-6. Recall from Chapter 3 that none of the estimated parameters were sufficient to predict the magnitude of sorption observed at $f_c > 0.4$ (assuming no methanol enhancement of benzoate solubility, i.e., $\sigma_i \approx 0$) (See Figure 3-3). From the data in Figure 4-6 and predictions given in Figure 3-3, we can deduce that the enhanced sorption of benzoic acid primarily results from some additional sorption mechanism of benzoate. However, in neat methanol, neutral benzoic acid may also contribute significantly to the enhance sorption. Note that positive deviations from log-linear behavior were observed at $f_c > 0.75$ and particularly in neat methanol (Figure 4-5). Similar deviations were noted for PCP sorption (see Figure 3-6), but to a lesser extent.

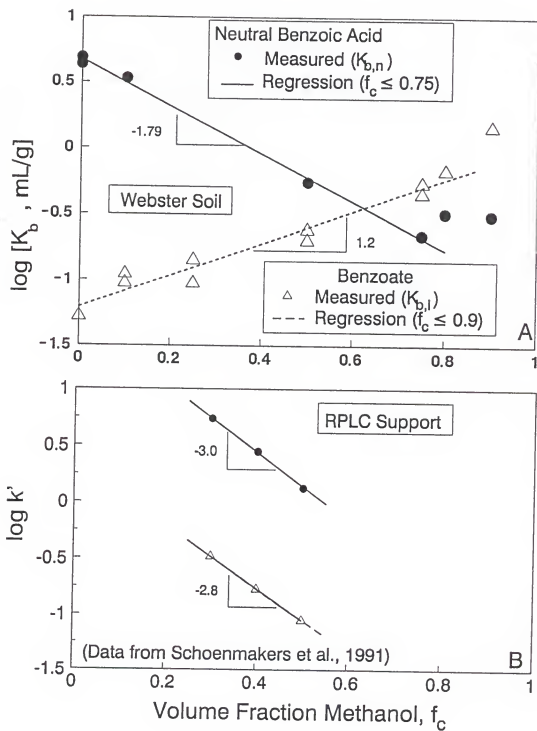


Figure 4-6. Sorption data obtained for neutral benzoic acid and benzoate as a function of methanol content.

Soil-solution pH^{app}

The substantial deviation from the log-linear model in neat methanol was attributed to sorption of neutral benzoic acid based on the assumption that pH^{app} was an adequate estimator of the soil-solution pH. Recall from Chapter 3 that the differences between measured pH (pH^{app}) and the calculated pH of 0.001 N HCl in methanol/water solutions (δ) were negligible for $f_c \leq 0.8$. For $f_c = 0.8, 0.9$, and 1.0, δ values of approximately 0.1, 0.4, and 2.3 pH units were observed, respectively. If we applied similar corrections to the pH^{app} measured for the soil solutions, the fraction of benzoic acid that is neutral is only affected in the neat methanol solutions. In neat methanol, the corrected pH (9) is approximately the same as the measured pK_a' (8.95) for benzoic acid, thus, $\phi_n = \phi_i \approx 0.5$ (e.g., $\text{pH} \approx \text{pK}_a'$). The point shown for neutral benzoic acid at $f_c = 1$ in Figure 4-6 is, therefore, really representative of a 50/50 mixture of neutral and ionized benzoic acid. This would offer an explanation for the apparent deviation at $f_c = 1$ from the relationship observed between neutral benzoic acid sorption and volume fraction methanol at $f_c < 0.9$. Even though there is some uncertainty about the pH and pK_a' measurements at $f_c \geq 0.9$, the magnitude of benzoic acid sorption observed in methanol/water (0.01 N CaCl_2) solutions is also greater than that predicted by Eq. (3-6) at lower f_c values where this uncertainty is small.

Effect of pH Treatments

The potential for the pH treatments of the soil to significantly change other soil properties must be considered. As previously noted, there was no measurable change in the OC content with treatment; however, a change in speciation of the

organic matter groups is expected. The CEC for the soil treated at the lowest pH was significantly lower than that observed for the other soils [30 cmol(+)/kg compared to 40 cmol(+)/kg]. A decrease in CEC with decreasing pH is expected for charge that originates from constant potential surfaces represented by organic matter; however, this soil also contains almost 30% clay (predominately montmorillonite) which is responsible for a substantial portion of the measured CEC. Overall the CEC is not considered a significant parameter in predicting the behavior of organic acids; however, this does suggest that washing the soils with an acidic solution may have dissolved some of the soil constituents (i.e, silica, aluminum and iron oxides, and related substituents). The elemental analysis given in Table 4-2 for the treated soils could suggest that dissolution of soil constituents did occur with the soil treated at the lowest pH having the lowest elemental concentrations. However, this trend may not be significant given the small soil sample size and the large dilution factors used in the analysis. Also, trends within each element (metals or silica) are approximately the same further suggesting that the observed differences are due to experimental errors. Note that even if substantial changes did occur to the soil with treatment, the impact of these changes appear to be a function of f_c .

Sorption Domains

Horvath et al. (1977) showed that hydrophobic interaction play a dominant role in determining interaction energies between both HOCs and HIOCs and reversed-phase chromatographic supports; however, sorption of benzoic acid by soils from methanol/water solutions were not predictable by only considering hydrophobic

interactions. To elucidate the sorption process of importance and get an indication of what specific domains of the soil might be most significant, sorption of benzoic acid by a range of sorbents was measured from aqueous and neat methanol solutions. The following sorbents were utilized: Pahokee muck, Ca-montmorillonite (SAz-1), Al_2O_3 , and $\text{Al}(\text{OH})_3$. The SAz-1 was a reference clay obtained from the clay depository in Clay Bank, NE [CEC of 120 cmol(+)/kg and specific surface area by N_2 BET of 100 m^2/g (Rao et al., 1988)]; Al_2O_3 and $\text{Al}(\text{OH})_3$ were obtained from Fisher; and Pahokee muck was sampled from Belle Glade, Florida [CEC of 136 cmol(+)/kg, and 38% OC (IFAS, 1974)]. Sorption was measured over a similar benzoic acid concentration range with a background electrolyte of 0.01 N CaCl_2 as used previously for the Webster soil experiments with a mass to volume ratio of two and a soil-solution pH between 7 and 8. In aqueous solutions, either negligible or negative sorption was observed by all sorbents at the measured pH. Similar results were obtained for benzoic acid in aqueous solutions by Bailey et al. (1968) for Na- and H-saturated montmorillonite; however, Carringer et al. (1975) was able to measure some adsorption of benzoic acid onto Ca-saturated montmorillonite at pH=6.

In neat methanol, sorption increased for all sorbents with the muck having the greatest sorption capacity at the pH investigated. Recall that in all the experiments presented in this work, the neat methanol actually contained 0.05% water, and all sorbents were air-dried, not oven dried. Estimates of the K values for the muck, Al_2O_3 , $\text{Al}(\text{OH})_3$, and SAz-1 were approximately 10, 0.8, 0.5, and 0.2 mL/g, respectively. Isotherm data are shown in Figure 4-7 along with the linear and

Freundlich fits. The results from this wide range of sorbents are similar to that observed for both Webster and Eustis soils; the addition of methanol enhanced sorption. The greater sorption by the muck suggests that sorption in the organic matter domain still might be of greatest importance, even though hydrophobic interactions alone were not sufficient to describe the sorption of benzoic acid by Webster soil.

Organic matter, especially the muck soil, also has a considerable amount of CEC sites. Given that these studies were conducted in 0.01 N CaCl_2 , most of the exchange sites were occupied by Ca^{+2} . From the previous experiment, the Ca^{+2} -saturated system resulted in enhanced sorption of benzoic acid upon methanol addition, whereas the K^{+} -saturated system did not. If we assume that methanol enhanced sorption in the presence of CaCl_2 is due to the solution-phase formation and exchange of positively charged ion-pairs, then sorption by SAz-1 would have been expected to be much greater than that observed (i.e., muck and SAz-1 have similar CEC). This apparent contradiction is similar to that implied in Chapter 3 when comparing the inferences from the results of increasing CaCl_2 concentrations versus the differences observed between Ca^{+2} - and K^{+} -saturated Webster soil. Likewise, these data further suggests the presence of another mechanism that is impacted by cation-type, but not necessarily the formation and exchange of positively-charged ion-pairs.

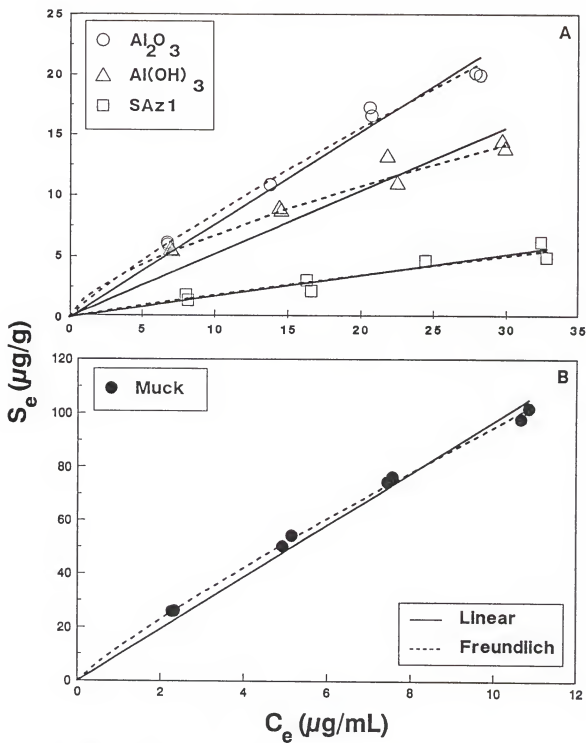


Figure 4-7. Isotherm data for benzoic acid on (A) Al_2O_3 , $\text{Al}(\text{OH})_3$, and SAZ-1 (pH \approx 8); and (B) Pahoee muck (pH \approx 7) along with linear and Freundlich fits.

Kummert and Stumm (1980) have extensively investigated the surface complexation of organic acids by aluminum oxides from aqueous solutions. As discussed in Chapter 3, ion-pair formation is enhanced upon addition of a solvent of lower dielectric constant. Likewise, complexation of an organic acid with structural metal cations may also be enhanced. To specifically assess the role of aluminum and iron oxides from a natural material in the presence of methanol and in the absence of organic matter, sorption of benzoic acid by sandy aquifer material (sampled from the Canadian Forces Base Borden in southern Ontario, Canada) was measured in several methanol/water solutions. Comparing sorption of benzoic acid between the Borden aquifer material and the Webster soil may help assess the role of metal oxides on the sorption of benzoic acid. The Borden material has been well characterized by Ball et al. (1990) (CEC of $0.7 \text{ cmol}(+)/\text{kg}$, specific surface area by N_2BET of $0.5 \text{ m}^2/\text{g}$). Substantial quantities of iron and aluminum oxides are present in the Borden material as coatings on the sand grains. Elemental analysis for this material was done in a similar manner as that for the untreated Webster soil. Relative to the Webster silty loam, this soil had 2, 3, and 4 times higher concentrations of K, Na, and Ca, respectively, and approximately the same amounts of Fe and Al; however, this particular subsample had only 0.02% OC content. Benzoic acid sorption by the Borden material increased from less than 0.005 mL/g to approximately 0.1 mL/g with f_c increasing from 0.2 to 0.8. At similar pH^{app} values (~ 7), sorption by Webster soil at $f_c=0.8$ was an order of magnitude higher (factor of 10), suggesting that the solute-solvent interaction with organic matter or organic

matter-clay matrix is predominant over than that with the metal oxides. Note, however, that the sorption coefficients reported here are in units of mL/g. Comparison of benzoic acid sorption normalized to surface area (N_2 BET) for the two materials would be closer in magnitude given that the Webster soil probably has ten times more surface area than the Borden aquifer material.

Summary

The impact of changes in soil-solution pH within a given solvent/water fraction was investigated to better differentiate and elucidate the roles of the ionized and neutral species on the overall sorption of carboxylic acids by soils. Sorption of benzoic acid by a silty clay loam was measured from several methanol/water solutions buffered at different pH values. Sorption of neutral benzoic acid was observed to decrease with increasing f_c in methanol/water solutions with 0.01 N $CaCl_2$, while benzoate sorption increased. This resulted in the sorption of benzoic acid decreasing with increasing pH at $f_c \leq 0.5$, while sorption increased with increasing pH at $f_c \geq 0.75$. A similar increase with increasing pH was observed for PCP in neat methanol, whereas PCP sorption decreased with pH $f_c = 0.75$ as observed in aqueous solutions. However, retention of both neutral and ionized benzoic acid by RPLC supports decreased with increasing methanol contents. Mobile phases buffered with solutions containing monovalent counter ions were employed in the RPLC analysis, whereas Ca^{+2} dominated the soil systems investigated indicating the importance of the cation-type in the sorption process.

Several explanations were proposed for the observed trends in data for sorption of organic acids by soils from mixed solvents. The enhanced retention of benzoic acid by soils upon addition of methanol appears to be due to some sorption involving benzoate and Ca^{+2} . Additional mechanisms did not to be invoked to explain benzoic acid retention by RPLC supports from methanol/water solutions where the buffer counterion was Na^{+} reflecting the importance of the cation in the retention process and/or the increased functionality of soil surfaces. Although the formation and exchange of positively-charged ion pairs is plausible, a preliminary assessment of several sorbents suggested the role of additional sorption mechanisms especially those equally impacted by cation-type. The use other types of cosolvents with similar or lower dielectric constants may help to further elucidate the plausibility of this ion-pairing phenomenon, since it is correlated to the decrease in the electropertmittivity of a solvent (Reichardt, 1990).

The magnitude of benzoic acid sorption measured for the various sorbents also suggests that the predominate sorbent fraction of interest still may be organic matter as conceptualized for HOCs. For the sorption of HOCs, the hydrophobic attributes of soil organic matter are presumed to be of greatest importance in retention by soils consistent with the many correlations observed between the retention of HOCs by soils and hydrophobic RPLC. Such results support the need to consider attributes other than the hydrophobic nature of organic matter, and specific solvent-sorbent interactions to explain the enhanced sorption of benzoic acid by soils.

The effect of solvent structure and solute-solvent interactions on equilibrium and rate constants are poorly understood. The problem begins with an inadequate understanding of water structure (Eisenberg and Kauzmann, 1969), and is further complicated by the addition of an organic cosolvent. How then may we begin to understand and interpret solvent-sorbent interactions, and solute-sorbent interactions in the presence of a cosolvent? The differences observed in the sorptive behavior of HOCs, phenolic compounds, and carboxylic acids in soil-mixed solvent solutions suggests that different solutes should be used to probe solvent-sorbent interactions. The use of different organic cosolvents, given the same solute, may also help to recognize, and possibly understand, the specificity of these solvent-sorbent interactions. Therefore, an investigation of the effect of solute structure for carboxylic acids (e.g., acidity and hydrophobicity) on sorption by soil in methanol/water solutions was initiated along with similar studies for benzoic acid using several solvents varying in a wide range of properties. These data are presented in the next chapter.

CHAPTER 5

IMPACT OF SOLUTE STRUCTURE AND ORGANIC COSOLVENTS ON THE SORPTION OF CARBOXYLIC ACIDS BY SOILS FROM MIXED SOLVENTS

Introduction

Investigations of the pH and cosolvent dependence of benzoic acid sorption by soils (Chapter 4) suggested that the enhanced sorption observed in methanol/water (0.01 N CaCl_2) solutions may be due to either (1) methanol-enhanced electrostatic interactions of benzoate with soil organic matter, or (2) the formation and exchange of positively-charged ion-pairs. To better distinguish between specific and nonspecific solvent interactions, sorption of benzoic acid by Webster soil was measured from binary mixtures of water and several organic cosolvents. Cosolvents were chosen that were miscible with water and spanned a range of bulk solvent properties.

In conjunction with an investigation on the role of the cosolvent on benzoic acid sorption, a similar investigation seemed warranted on the role of solute acidity on sorption, especially given that methanol additions did not appear to enhance sorption of substituted phenols (Chapter 3). Carboxylic acids are more acidic than phenols and have a greater propensity for hydrogen bonding. Therefore, sorption by Webster soil of several substituted benzoic acids varying in acidity (pK_a) and hydrophobicity ($\log K_{ow}$) was measured from methanol/water solutions. For both the

ionized and neutral forms of the carboxylic acids $\log K_{ow}$ values were also measured for use as indicators of relative hydrophobicities. Correlation of the sorption profiles for the different substituted acids with indices of acidity and hydrophobicity will be attempted. A hypothesis for the enhanced sorption of carboxylic acids in the presence of methanol will be deduced by assimilating the results already discussed in Chapters 3 and 4 with those presented in this chapter.

Materials and Methods

Sorbents

The sorbent used in this study was a sample of Webster silty clay loam (Typic Haplaquoll) from Iowa, similar in sand, silt, and clay contents to the soil sample described in Chapter 3 and 4. The organic carbon (OC) content was slightly higher (3.12%) and the soil-solution pH in 0.01 N CaCl_2 was lower (5.8). The soil was air-dried and passed through a 2 mm sieve prior to use.

Chemicals

The organic solvents and organic acids used in this study are listed in Tables 5-1 and 5-2, respectively, along with selected physical and chemical properties. Solvents were purchased from either J.T. Baker (high purity, HPLC grade) or Aldrich Chemical Co. (purity >99%), and used without further preparation with the exception of octanol. Benzoic acid was purchased from Fisher Scientific (purity >99%) and all other crystalline compounds were purchased from Aldrich Chemical Co. (purity of >99%). Some of the benzoic acid experiments employed ^{14}C material

(uniformly ring-labeled) with a specific activity of 13.3 mCi/mmol, purchased from Sigma Chemical Co., with a reported purity of >98%.

Table 5-1. List of various chemical and physical properties of solvents.

Parameter	Acetone	Acetonitrile	DMSO	Methanol	1,4 Dioxane
Boiling Point (°C) ^a	56	81.6	189	64.96	101.2
log K _{ow} ^b	-0.24	-0.34	-2.03	-0.82	-0.42
Density (g/mL) ^a	0.788	0.786	1.101	0.792	1.03
Hildebrand Solubility ^b Parameter(MPa ^{-1/2})	20.2	24.3	24.5	29.6	20.5
Surface Tension (dyne/cm) ^a	26.3	29.6	43.5	24	36.2
Hydrogen Bond Donor ^c	0	NA ⁱ	0	24.6	NA
Hydrogen Bond Acceptor ^c	27.12	18.27	28.2	49.2	NA
Viscosity (mN s m ⁻²) ^a	0.34	0.375	2	0.54	1.2
Refractive Index ^a	1.35	1.34	1.48	1.33	1.422
Dielectric constant ^a	20.7	37.5	47	32.7	2.2
Dipole moment (D) ^a	2.88	2.7	3.9	1.66	
E _T (30) (kcal/mole) ^b	42.2	45.6	45	55.4	36
Donor No. (kcal/mole) ^d	17	14.1	29.8	19	14.8
Acceptor No. (kcal/mole) ^b	12.5	18.9	19.3	41.5	10.8
σ _n ^e	3	2.74	2.96	2.25	3.3 ^g
pK _{a,s} ^h (Benzoic Acid) ^h	18.2	20.7	8.7	8.96	NA

^a Dean (1972); ^b Reichardt (1990); ^c Yalkowsky, 1985; ^d Marcus, 1984; ^e NA means not available; ^f Estimated by a log-linear regression of solubility versus volume fraction cosolvent ($f_c=0$ to 0.8) with a force fit through the aqueous solubility; ^g estimated by adding the difference observed between σ values for anthracene in DMSO/water and 1,4-dioxane/water solutions (Pinal et al., 1990) to the σ_n value for benzoic acid in DMSO/water solutions; Ludwig et al., 1986; ⁱ Not Available

Table 5-2. List of various chemical and physical properties of solutes.

Compound	pK _{a,w}	Aqueous Solubility (mg/L)
benzoic acid	4.2 ^a	3,000
2-naphthoic acid	4.6 ^a	58 ^g
9-anthroic acid	3.65 ^a	63 ^b
o-chlorobenzoic acid	2.94 ^a	2,100
m-chlorobenzoic acid	3.84 ^a	400
p-chlorobenzoic acid	4. ^a	77
2,4-dichlorobenzoic acid	2.85 ^b , 2.68 ^f , 2.75 ^f	NA ^c
2,5-dichlorobenzoic acid	2.61 ^b , 2.47 ^f	NA
2,6-dichlorobenzoic acid	1.49 ^b ; 1.59 ^f	NA
2,4,6-trichlorobenzoic acid	1.24 ^{b,c}	NA

^a Perrin, (1972); ^b Measured; ^c Values uncertain; ^d Levitan and Barker (1972); ^e not available; ^f Serjeant and Boyd (1979); ^g Stephen (1963).

Equilibrium Sorption Isotherms

Equilibrium sorption isotherms were measured using the same batch-equilibration method as described in Chapters 3 and 4. A soil mass to solution volume ratio of either 1:1 or 1:2 was used in all studies. All solutions used had a 0.01 N CaCl₂ matrix. Initial solution concentrations added to the soils ranged from

10 to 40 $\mu\text{g/mL}$ for all solutes. All sorption isotherms were measured at room temperature ($T=20\text{-}24^\circ\text{C}$). Following equilibration, the solution and solid phases were separated by centrifuging the soil samples at approximately 300 RCF (relative centrifugal force) using a Sorvall RT6000 centrifuge.

Each isotherm consisted of sorption measured in duplicate at four concentrations. Also for each isotherm, blanks containing the solvent with and without soil were run to check for coelution of chromatographic peaks resulting from dissolved soil components or to obtain an appropriate background count in the LSC analysis. Samples were equilibrated by rotating for 16-24 hours. Nonradiolabelled samples were analyzed by RPLC techniques as described previously in Chapter 3, and radiolabeled samples were analyzed by liquid scintillation counting (LSC) techniques as previously described in Chapter 4. For the RPLC analysis of each of the substituted carboxylic acids, the mobile phase composition was varied to maximize separation and minimize elution time. Sorption coefficients, K (mL/g), were estimated by difference from initial and equilibrium solute concentration data as previously described in Chapter 3.

Determination of Octanol-Water Partition Coefficients

Octanol-water partition coefficients were individually determined for the neutral and ionized species for each of the substituted carboxylic acids listed in Table 5-2. Approximately 1 mL of double-distilled octanol containing 200 to 500 mg/L of a single solute was added to 25 mL of pH-adjusted aqueous solution in 35 mL borosilicate Kimax centrifuge tubes. Samples were equilibrated overnight on a rotator, followed by centrifugation at 300 RCF for 25 minutes. Aliquots of the

octanol phase (0.5 mL) were then taken and added to 0.5 mL aliquots of methanol for RPLC analysis. After removal of the remaining octanol from the aqueous phase, 1 mL aliquots of the aqueous phase were added to 0.5 mL methanol aliquots for RPLC analysis. Following aliquots for analysis, pH measurements of the remaining aqueous phase were made using a Fisher Accumet Model 925 pH meter and an Ingold micro-electrode (AgCl saturated 3 M KCl filling solution).

Results and Discussion

Sorption of benzoic acid by Webster soil was measured in different solvent/water solutions to investigate the impact of solvent type. In addition, sorption of several substituted benzoic acids by Webster soil was measured in methanol/water solutions to investigate the role of solute acidity and hydrophobicity. Linear approximations of the sorption coefficients (K_b) were considered adequate for this preliminary assessment of the effect of solvent and solute structure on carboxylic acid sorption; however, nonlinearity was noted in some of the solute/solvent/water combinations. Although linear estimates of K_b given in Tables 5-3 and 5-4 will be used in comparing the impact of the different solvents and solutes, respectively, the Freundlich fit to the isotherm data is also given. Nkedi-Kizza et al. (1985) had noted increased isotherm linearity with increasing f_c ; however, no consistent trend is apparent for the isotherm data given in Tables 5-3 and 5-4. Representative isotherms along with linear fits for sorption of benzoic acid in several solvent/water mixtures and for sorption of substituted carboxylic acids in methanol/water solutions are shown in Figures 5-1 and 5-2, respectively.

Table 5-3. Parameters for linear and Freundlich fits to the isotherm data for benzoic acid in several solvent/water solutions.

Solvent	f_c	$K_d(\text{mL/g})$	$K_f(\text{mL}^N \mu\text{g}^{1-N} \text{g}^{-1})$	$N \pm \text{SE}^a$
Acetone	0.2	0.177	0.030	0.84 ± 0.06
	0.4	0.264	0.285	0.97 ± 0.05
	0.6	0.175	0.305	0.83 ± 0.06
	0.8	0.111	0.088	1.06 ± 0.07
DMSO	0.2	0.239	0.732	0.66 ± 0.02
	0.25	0.256	0.57	0.75 ± 0.05
	0.4	0.296	0.455	0.87 ± 0.03
	0.5	0.385	0.515	0.90 ± 0.05
	0.6	0.507	0.724	0.88 ± 0.04
	0.75	0.845	0.872	0.87 ± 0.03
	0.8	0.872	1.267	0.87 ± 0.03
	0.8	0.872	1.267	0.87 ± 0.03
Acetonitrile	0.2	0.173	0.263	0.88 ± 0.06
	0.25	0.167	0.153	1.01 ± 0.11
	0.4	0.165	0.181	0.98 ± 0.07
	0.5	0.14	0.162	0.95 ± 0.09
	0.6	0.146	0.183	0.92 ± 0.07
	0.75	0.12	0.182	0.84 ± 0.11
	0.8	0.113	0.118	0.99 ± 0.03
	0.8	0.113	0.118	0.99 ± 0.03
1,4-Dioxane	0.2	0.23	0.32	0.88 ± 0.06
	0.25	0.24	0.42	0.83 ± 0.01
	0.4	0.28	0.44	0.85 ± 0.04
	0.5	0.29	0.379	0.91 ± 0.05
	0.6	0.23	0.25	0.95 ± 0.06
	0.75	0.137	0.198	0.89 ± 0.07
	0.8	0.14	0.16	0.94 ± 0.13
	0.8	0.14	0.16	0.94 ± 0.13

^a Standard Error

Table 5-4. Parameters for linear and Freundlich fits to the isotherm data for substituted benzoic acids in methanol/water solutions.

Solvent	f_c	$K_d(\text{mL/g})$	$K_f(\text{mL}^N \mu\text{g}^{1-N} \text{g}^{-1})$	$N \pm \text{SE}^a$
Benzoic acid ^b	0	0.12	0.07	1.10±0.06
	0.1	0.11	0.13	0.89±0.21
	0.2	0.09	0.04	1.24±0.06
	0.4	0.15	0.09	1.17±0.02
	0.5	0.2	0.12	1.16±0.05
	0.6	0.30	0.26	1.05±0.12
	0.75	0.56	0.37	1.16±0.05
	0.8	0.82	1.33	0.85±0.03
	0.9	1.69	2.5	0.86±0.04
	1.0	4.98	8.13	0.79±0.01
Anthroic acid	0	2.58	4.37	0.71±0.02
	0.2	1.98	2.35	0.91±0.08
	0.4	1.20	2.28	0.67±0.10
	0.6	1.17	2.35	0.66±0.05
	1	5.79	8.00	0.79±0.01
Naphthoic acid	0	5.16	9.83	0.58±0.03
	0.2	3.26	6.35	0.64±0.05
	0.4	2.17	3.67	0.74±0.08
	0.6	1.60	2.35	0.82±0.05
	0.8	1.99	2.81	0.84±0.02
	1.0	9.91	11.72	0.77±0.02

(Table 5-4 continued)

(Table 5-4 continued)

Solvent	f_c	$K_d(\text{mL/g})$	$K_f(\text{mL}^N \mu\text{g}^{1-N} \text{g}^{-1})$	$N \pm \text{SE}^a$
2,4,6-trichlorobenzoic acid	0	0.11	0.10	1.02±0.09
	0.2	0.07	0.05	1.12±0.13
	0.4	0.07	0.18	0.65±0.32
	0.6	0.11	0.24	0.73±0.10
	0.8	0.15	0.20	0.90±0.05
	1	0.99	0.88	1.04±0.05
2,4-dichlorobenzoic acid	0	0.25	0.40	0.83±0.04
	0.2	0.19	0.50	0.64±0.08
	0.4	0.17	0.28	0.82±0.02
	0.6	0.22	0.15	1.16±0.04
	0.8	0.43	0.42	1.01±0.04
	1	2.75	2.94	0.96±0.03
2,5-dichlorobenzoic acid	0	0.19	0.45	0.64±0.09
	0.2	0.11	0.20	0.78±0.07
	0.4	0.11	0.12	1.00±0.07
	0.6	0.15	0.02	1.82±0.15
	0.8	0.34	0.28	1.08±0.08
	1	2.22	2.53	0.92±0.06
2,6-dichlorobenzoic acid	0.4	0.04	0.04	1.00±0.18
	0.6	0.09	0.13	0.86±0.12
	0.8	0.23	0.44	0.75±0.06
	1	1.29	1.10	1.08±0.05

^a Standard Error^b This Webster sample was obtained from the Webster site at a different time.

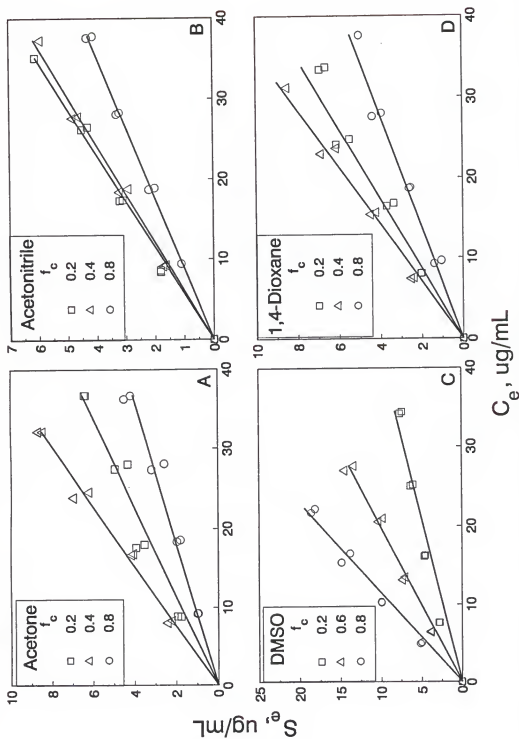


Figure 5-1. Representative isotherms for benzoic acid in (A) acetone/water; (B) acetonitrile/water; (C) DMSO/water; and (D) 1,4-dioxane/water solutions.

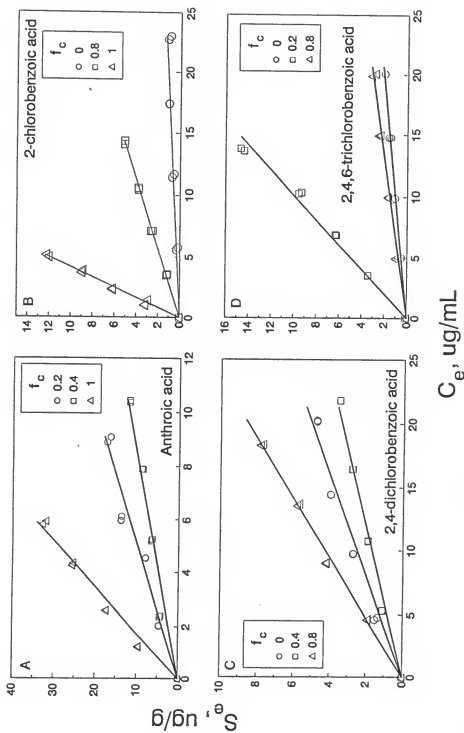


Figure 5-2. Representative isotherms for (A) anthroic acid; (B) 2-chlorobenzoic acid; (C) 2,4-dichlorobenzoic acid; and (D) 2,4,6-trichlorobenzoic acid in various methanol/water solutions.

Sorption of Benzoic Acid in Several Solvent/Water Solutions

To investigate if specific solvent properties were responsible for the enhanced sorption of benzoic acid observed upon addition of methanol, benzoic acid sorption was measured in additional binary mixtures of water and several other organic solvents spanning a wide range of solvent properties. Addition of any of the solvents chosen will cause an increase in benzoic acid solubility relative to that in water. Data for benzoic acid solubility in binary mixtures are available for all but 1,4-dioxane/water solutions, and are shown in Figure 5-3A.

All the cosolvents chosen have dielectric constants lower than that of water; therefore, in each case addition of a solvent would enhance the potential for ion-pairing. A summary of the sorption coefficients estimated from the batch equilibration studies as a function of volume fraction cosolvent (f_c) in different binary mixtures is given in Figure 5-3B. Sorption of benzoic acid from DMSO/water solutions is very similar in direction and magnitude to that observed in methanol/water solutions. The remaining solvent/water mixtures (e.g., acetone, acetonitrile, and 1,4-dioxane) all display a parabolic shaped curve with an apparent sorption maximum at an approximate volume fraction of 0.4 to 0.5. The lack of relationship between the observed sorption trends and the cosolvent's dielectric constant appears to discount the formation and exchange of positively charged ion-pairs. Recall from Chapter 3 that this mechanism was proposed to explain the differences in benzoic acid sorption by K^+ - versus Ca^{+} -saturated Webster soil. These results suggest the need to invoke alternate sorption mechanisms that may also be impacted by cation-type such as cation- and water-bridging, and hydrogen bonding.

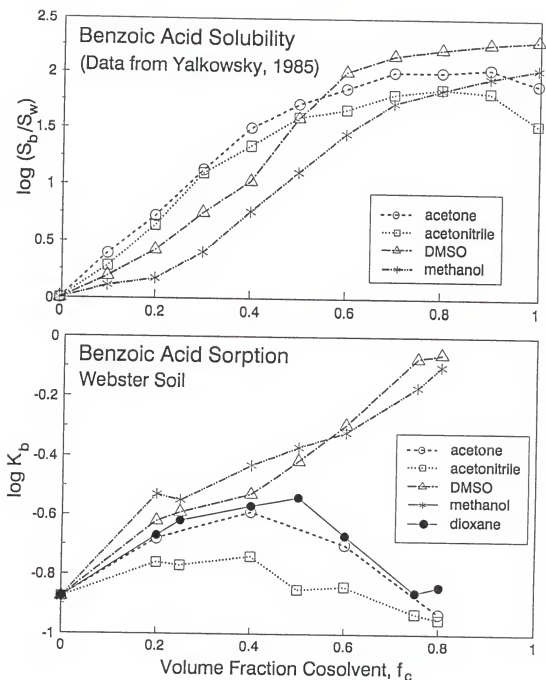


Figure 5-3. (A) Benzoic acid solubility data where S_b and S_w are solubilities in the binary solution and water, respectively; and (B) benzoic sorption data with Webster soil in binary mixtures of water and several organic cosolvents as a function of volume fraction cosolvent (f_c).

Trends in soil-solution pH (pH^{app}) measured in binary mixtures of water and several organic cosolvents are shown in Figure 5-4. Decreases in pH^{app} with increasing f_c were observed for all solvents except DMSO. The actual decrease in pH^{app} observed between aqueous solutions and $f_c=0.8$ were 0.3, 0.8, 0.9, and 1.1 pH units for methanol, 1,4-dioxane, acetone, and acetonitrile, respectively. For DMSO/water solutions, increases in pH^{app} of almost 2 pH units were observed going from aqueous solutions to $f_c=0.8$. At first, the accuracy of pH^{app} may be questioned; however, Rubino and Berryhill (1986) observed changes of only 0.5 pH units in their measurements of 0.01 N HCl in aqueous and 50/50 DMSO/water solutions using a glass electrode similar to the one used in this study. Therefore, a majority of the change observed in soil-suspension pH with DMSO/water solutions may be due to a specific reaction of the solvent with the sorbent in which hydroxide ions are released.

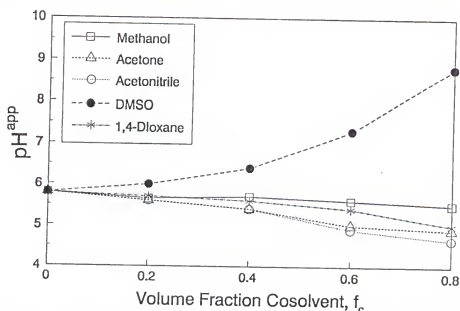


Figure 5-4. Trends in soil-solution pH^{app} measured in binary mixtures of water and several organic cosolvents.

To assess the presence or absence of specific solvent interactions among the different cosolvents, Eq. (3-6) was employed in a similar manner as previously applied to the data for sorption of organic acids from methanol/water solutions (Chapter 3). Recall that Eq. (3-6) was a first attempt to incorporate cosolvency phenomena in terms of solubility and cosolvent-induced speciation effects in order to explain the observed sorption. The organic cosolvents used in this study vary in their cosolvency power (see Figure 5-4 and σ values in Table 5-1) and in their impact on conditional ionization constants (pK_a') (see Table 5-1). Of the parameters needed to apply Eq. (3-6), $K_{w,n}$ and $K_{w,i}$ were the same as used previously for benzoic acid in Chapter 3; apparent pH values (pH^{app}) were used to estimate soil-solution pH; σ_n values were obtained from solubility data as given in Table 5-1; an α_n value of 0.8 was used as previously estimated from the benzoic acid sorption and solubility data measured in methanol/water solutions (Chapter 4) was used; and $\alpha_i\sigma_i$ was set equal to zero.

The pK_a' values were estimated using a the following modified Born equation,

$$pK_{a,s} = \frac{Ne^2}{RT} \left(\frac{1}{r_H} + \frac{1}{r_A} \right) \left(\frac{1}{\epsilon_e} - \frac{1}{\epsilon_w} \right) + pK_{a,w} + \Delta \quad (5-1)$$

where N is Avogadro's number; e is the electronic charge; R is the gas constant; T is temperature; r_H and r_A are the radii of hydronium and organic ion, respectively; ϵ_e and ϵ_w are the cosolvent and water dielectric constants, respectively; and Δ is an estimate for nonelectrostatic medium effects. The dielectric constant needed at each

f_c was estimated assuming a linear combination of the weighted fractions [e.g., $f_c \epsilon_s + (1-f_c) \epsilon_w$] (Franks and Ives, 1966). The effect of solvent composition on an acid's pK_a' can be expressed in terms of electrostatic and nonelectrostatic medium effects (Popovych and Tomkins, 1981). The electrostatic contribution to the medium effect (e.g., ability of a solvent to separate charged species in solution) can be represented by the Born equation. The nonelectrostatic portion of the medium effect represents the difference between cohesive and adhesive forces between the solute and solvent species, assuming all solute species are uncharged. Rubino and Berryhill (1986) suggested taking the difference between measured pK_a' values and those calculated using the Born equation in order to estimate the contribution of the nonelectrostatic medium effects (Δ). Therefore, to better estimate pK_a' values in the various binary mixtures, nonelectrostatic medium effects (Δ) were estimated by using Δ values estimated from methanol/water solutions in the manner suggested by Rubino and Berryhill (1986).

Equation (3-6) predictions for sorption of benzoic acid in the different binary mixtures using the parameters as just described are shown in Figure 5-5 along with the measured data. In acetone/water, acetonitrile/water solutions and dioxane/water solutions, Eq. (3-6) does a reasonable job in estimating the observed benzoic acid sorption. These data suggests that for some solvent/water systems, Eq. (3-6) may be adequate to predict sorption of organic acids. However, a very poor prediction resulted from application of Eq. (3-6) to the sorption of benzoic acid in DMSO/water solutions similar to that observed in methanol/water solutions.

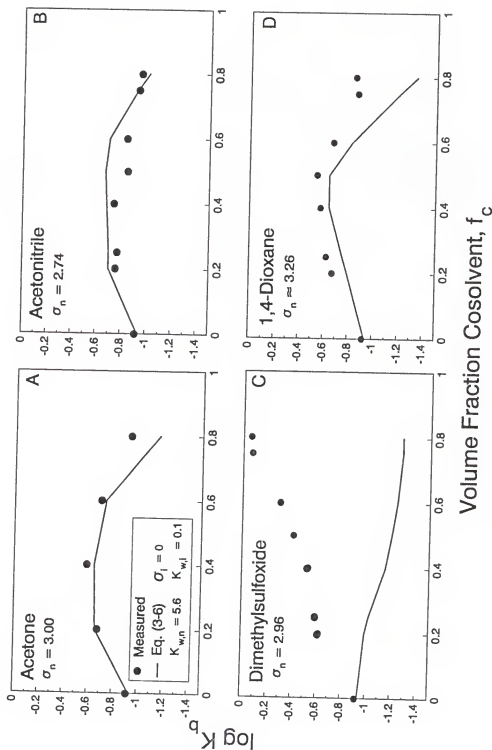


Figure 5-5. Measured and predicted (Eq. 3-6) sorption of benzoic acid by Webster soil from (A) acetone/water; (B) acetonitrile/water; (C) DMSO/water; and (D) 1,4-dioxane/water solutions as a function of volume fraction cosolvent (f_c).

Similar observations in methanol/water and in DMSO/water solutions (i.e., magnitude of sorption and large deviations from Eq. (3-6) predictions) leads to a search for some common solvent property that may explain such behavior. However, upon reviewing various solvent parameters summarized by Reichardt (1990)(see Table 5-1 for a partial listing), a unique bulk solvent property could not be found which explains the similarity or dissimilarity observed in the shape of the sorption curves observed between different cosolvents. For example, acetone, acetonitrile, DMSO, and 1,4-dioxane are all dipolar aprotic solvents, whereas, methanol is an amphiprotic solvent. Of the aprotic solvents, DMSO is the solvent with a relatively high polarizability (as reflected in a high refractive index) and a high dielectric constant (ϵ_r) which may explain the dissimilarity observed with DMSO relative to the other aprotic solvents. However, this does not explain why similar sorption behavior was observed with methanol, since methanol has a lower refractive index than any of the solvents and a ϵ_r whose value is between that of acetone and acetonitrile. In terms of hydrogen bonding characteristics of the pure solvent as exhibited by hydrogen bond donor and acceptor numbers, only methanol can act as a hydrogen bond donor; however, methanol, DMSO, and acetone have a large ability to accept hydrogen bonds.

The inability to identify a single solvent property responsible for the varying behavior observed for the different solvent/water solutions suggest the contribution of some interaction not expressed by any one bulk solvent property. This suggests that: (1) although both methanol and DMSO have the same macroscopic effect on

sorption of benzoic acid, sorption is driven by two completely different mechanisms; (2) in the presence of water, one of the two solvents acquires a property common to the other solvent; and (3) *preferential* or *selective solvation* interactions.

For sorption of organic solutes from aqueous solutions, several mechanisms have been proposed in the literature, including hydrophobic interactions, London-van der Waals or dispersion forces, hydrogen bonding, cation and water bridging, cation and anion exchange, ligand exchange, protonation, covalent bonding or chemisorption, and interlayer adsorption. These mechanisms have not been assessed for mixed solvent systems; however, through a deductive process, inferences can be made from the data presented in this work regarding the relative importance of these mechanisms for sorption of organic acids by soils. Results presented here suggested the predominance of soil organic matter interactions, the significance of cation-type in the sorption process, the unlikelihood of formation and exchange of positively charged ion-pairs, and absence of chemisorption. Also, van der Waals forces can be assumed to be negligible considering the relatively small molecular size of the organic acids investigated, and the incorporation of hydrophobic interactions were found to be inadequate for describing the observed sorption. Therefore, only hydrogen bonding, and cation- or water-bridging interactions warrant further discussion.

As previously noted from bulk solvent properties, it appears that only methanol is capable of donating hydrogen bonds; however, there is spectroscopic evidence (Raman and infrared spectroscopy) that DMSO complexes with water

forming $\text{DMSO} \cdot (\text{H}_2\text{O})_2$ (Kelm et al., 1975); thus acquiring hydrogen-donating characteristics (Kelm et al., 1975; Bertoluzza et al., 1979; 1981). The opposing trends observed for the sorption of benzoic acid by Ca^{+2} - and K^{+} -saturated Webster soil is also consistent with a hydrogen bonding mechanism as previously discussed. Thus, hydrogen-bonding interactions as a potential explanation for the enhancement of benzoic acid sorption by soils is plausible, especially given the hydrogen-bonding nature of carboxylate groups (this includes solute and sorbent functional groups) and of methanol and $\text{DMSO} \cdot (\text{H}_2)_2$. The relevant question at this point is how could the addition of methanol or DMSO strengthen hydrogen-bonding interactions of the solute with the sorbent.

For sorption of HOCs from aqueous and mixed solvents, the bulk solution properties are considered to be the driving force (i.e., solute-solvent interactions) in the sorption process with stabilization occurring at the local scale (preferential interaction with organic matter regions). In the chromatographic literature regarding the retention of HOCs by RPLC supports, references are commonly made to the preferential solvation of the reversed-phase support with cosolvent molecules, but its significance is usually dismissed due to the predominance of bulk-scale solute-solvent interactions. Similar assumptions appear to also be adequate for retention of organic acids by the same RPLC supports. However, it is apparent from the sorption studies presented here that preferential or selective solvation may be of extreme importance for sorption of organic acids.

The term *solvation* refers to the surrounding of each dissolved molecule (or sorbent functional groups) by a shell of solvent molecules which are bound to some degree (i.e., long enough to experience the its translational movements) (Reichardt, 1990). Preferential or selective solvation comes about when more than one solvent is present and the composition of the solvent shell around a solute (or sorbent) is different than the composition of the bulk solution. Preferential solvation is a result of differences in the free energy of solvation (ΔG_{solv}) for a given solute and is induced by both nonspecific and specific solute-solvent interactions. Nonspecific solute-solvent associations are caused by a dielectric enrichment in the solvent shell of ions or dipolar molecules, and causes for specific solute-solvent associations include hydrogen-bonding or electron pair donating/accepting interactions (Reichardt, 1990). The preferential solvation of Ag^+ by acetonitrile in acetonitrile/water solutions is an example of specific solute-solvent associations resulting from electron pair donation (Strehlow and Koepp, 1958). Water molecules preferentially solvate both Ca^{+2} and Cl^- ions in methanol/water solutions as a result of electrostatic interactions causing a dielectric enrichment phenomena in the solvent shell (i.e., solvation sheath is enriched with the solvent of highest dielectric constant) (Schneider and Strehlow, 1962). Given the heterogeneity of both an organic acid and soil organic matter (i.e., mixture of hydrophobic and polar regions) it is not unreasonable to infer heterogeneity in the solvation shell about both solute and the sorbent (soil organic matter). In addition, preferential orientation of the molecules in the solvation shells are also expected. Selective solvation and preferential

orientation of the solvent molecules in the solvation shell coupled with hydrogen-bonding interactions may be the mechanisms responsible for the enhanced sorption of carboxylic acids by soils in methanol/water and DMSO/water solutions.

Sorption of Several Substituted Carboxylic Acids in Methanol/Water Solutions

From the foregoing discussion, it is clear that solvent structure plays a crucial role in the relationship between sorption and volume fraction cosolvent (f_c), but data presented in Chapter 3 indicated that solute structure is also important. Chapter 3 investigations showed that sorption of benzoic acid increased with increasing methanol fractions and was not predictable by incorporating cosolvent-enhanced solubility and cosolvent-induced speciation effects (Eq. 3-6) which had prompted further study. However, the sorption of several substituted phenols did decrease with increasing methanol fractions in a predictable manner similar to that observed for nonpolar hydrophobic organic chemicals. Carboxylic acids are generally more acidic than phenols, as indicated by the lower pK_a values, and have a greater propensity to hydrogen bond. Therefore, the role of solute structure on sorption of carboxylic acids by soils from solvent/water solutions was further investigated by measuring sorption from methanol/water solutions of several carboxylic acids. The acids were chosen by adding benzene rings or chlorine groups to benzoic acid resulting in carboxylic acids with varying degrees of acidity (e.g., pK_a) and hydrophobicity (e.g., K_{ow}).

First, the relative hydrophobicity of the ionized and neutral forms of the acids was assessed by measuring octanol/water partition coefficients (K_{ow}) of the various carboxylic acids in acidic ($pH < pK_a$) and basic solutions ($pH > pK_a$). The log K_{ow}

values for the ionized (i) and neutral (n) species are shown in Table 5-5 along with the pH measurements of the aqueous solutions after equilibration and aqueous ionization constants ($pK_{a,w}$) for comparison. The difference between measured $K_{ow,i}$ and $K_{ow,n}$ values becomes increasingly larger with increasing acidity. An attempt to correlate measured K_{ow} values and pK_a values with the sorption profiles observed in solvent/water solutions for these carboxylic acids follows.

Table 5-5. The logarithms of the octanol/water partition coefficients ($\log K_{ow}$) for both the neutral (subscript n) and ionized (subscript i) species of several substituted carboxylic acids.

Compound	$pK_{a,w}$	$\log K_{ow,n}^a$	pH^b	$\log K_{ow,i}$
benzoic acid	4.2 ^a	2.00	5.0	1.10
2-naphthoic acid	4.6 ^a	3.34	6.1	1.48
9-anthroic acid	3.65 ^a	3.5	5.4	1.27
o-chlorobenzoic acid	2.94 ^a	2.16	4.4	0.67
m-chlorobenzoic acid	3.84 ^a	2.79	5.3	1.52
p-chlorobenzoic acid	4. ^a	2.73	5.6	1.27
2,4-dichlorobenzoic acid	2.85 ^b	2.98	4.5	0.65
2,5-dichlorobenzoic acid	2.61 ^b	2.98	5.6	0.75
2,6-dichlorobenzoic acid	1.49 ^{b,c}	2.35	4.0	-0.14
2,4,6-trichlorobenzoic acid	1.24 ^{b,c}	3.07	4.6	-0.05

^a pH of aqueous solution ≤ 0.45 after equilibration.

^b pH of aqueous solution for ionized species (basic) after equilibration.

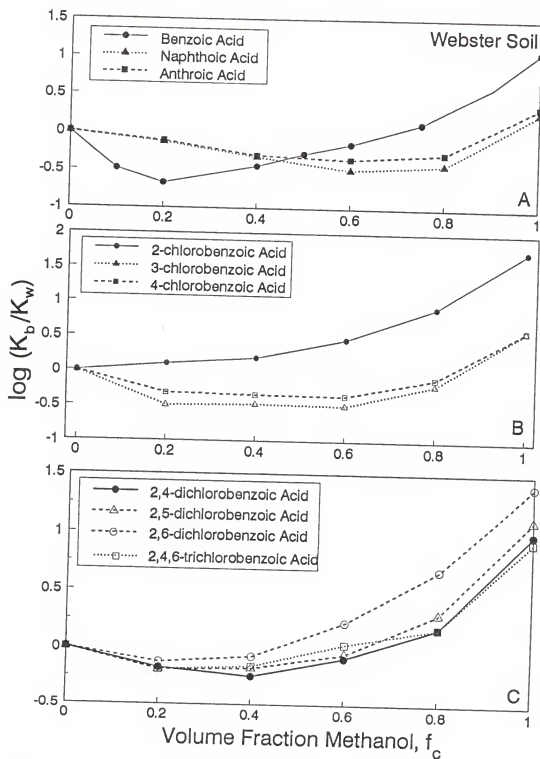


Figure 5-6. Normalized sorption coefficients, $\log (K_b/K_w)$, for the sorption of selected substituted carboxylic acids by Webster soil as a function of volume fraction methanol (f_c).

Normalized sorption coefficients, $\log (K_b/K_w)$, for the sorption of selected substituted carboxylic acids by Webster soil plotted as a function of volume fraction methanol (f_c) are shown in Figure 5-6. A tabulated form of this data and the Freundlich fits were given previously in Table 5-3. Sorption profiles for all the carboxylic acids investigated are similar to that observed for benzoic acid in methanol/water and DMSO/water solutions. Correlations of $\log K_{MeOH}$, $\log K_w$, and $pK_{a,w}$ with $\log K_{ow,n}$ are extremely poor ($r^2 < 0.35$), whereas similar correlations to $\log K_{ow,i}$ are much improved ($r^2 > 0.75$). Shown in Figure 5-7 is the correlation between $\log K_{MeOH}$ and the $\log K_{ow}$ values for both the ionized and neutral forms of the acids. Substantially better correlations observed with $K_{ow,i}$ values supports the argument that the carboxylate is the predominate species responsible for the enhanced carboxylic acid sorption by soils from methanol/water solutions.

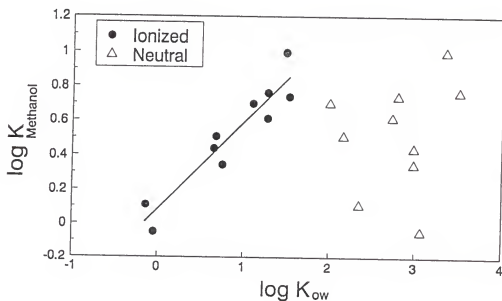


Figure 5-7. Correlation between benzoic acid sorption in neat methanol ($\log K_{MeOH}$) and the $\log K_{ow}$ values for both the ionized (i) and neutral (n) forms of the substituted carboxylic acids.

Summary

Sorption profiles observed for the sorption of benzoic acid by soils from methanol/water solutions (Chapter 3) could not be predicted by incorporating cosolvent enhanced solubility and cosolvent-induced speciation (Eq. 3-6) prompting an investigation of benzoic acid sorption in binary mixtures of water and several other organic solvents. The sorption of benzoic acid from DMSO/water solutions was found similar to that observed for methanol/water solutions; however, Eq. (3-6) was successfully applied to benzoic acid sorption in acetone/water, acetonitrile/water, and 1,4-dioxane/water solutions. No single parameter for describing bulk solvent properties could be used to explain the similarities and dissimilarities observed in benzoic acid sorption from different solvent/water systems. However, DMSO appears to acquire hydrogen donating characteristics similar to methanol by forming $\text{DMSO} \cdot (\text{H}_2\text{O}_2)$ complexes.

The importance of solute structure was also investigated by measuring the sorption of several substituted carboxylic acids by Webster soil from methanol/water solutions. Correlations of $\log K_{\text{MeOH}}$, $\log K_w$, and $\text{p}K_{a,w}$ with $\log K_{ow}$ values for both the ionized and neutral species consistently showed substantially better correlations with $K_{ow,i}$ values. This further supports the conclusion made in Chapter 4 that the carboxylate is the predominate species responsible for the enhanced carboxylic acid sorption by soils from methanol/water solutions. Similar observations were not observed for substituted phenols in methanol/water solutions (Chapter 3). Enhanced sorption of carboxylic acids appeared to be a function solute, solvent, and electrolyte

composition; therefore, it was deduced that hydrogen-bonding interactions coupled with preferential or selective solvation are the likely mechanisms of importance in this study.

CHAPTER 6 SUMMARY AND CONCLUSIONS

Complex Mixtures

Contamination of soils and water at waste disposal sites commonly involve various combinations of nonpolar or hydrophobic organic chemicals (HOCs) and hydrophobic ionogenic organic chemicals (HIOCs), as well as mixtures of water and one or more organic cosolvents (either completely or partially miscible in water). These mixtures may be considered complex based on the number of chemicals that constitute the mixture. On the other hand, complexity of a mixture can be defined by considering how the properties of the mixture deviate from some "ideal" behavior, regardless of the number of components. The former view corresponds to a mixture being *complex in composition*, whereas the latter implies *complexity in behavior*. The important point is that a mixture can be complex in composition without being complex in behavior and vice versa. In general terms, structurally similar chemicals are likely to form "ideal" mixtures. Emphasis of this work was on understanding the chemodynamics (e.g., solubility, sorption, and transport) of such complex mixtures. Experimental and theoretical analyses presented focus on: (1) liquid-liquid partitioning behavior of aromatic hydrocarbons between environmentally relevant organic immiscible liquids (OILs) and water; and (2) the solubility and sorption of HIOCs by soils from completely miscible-organic solvent/water mixtures.

Liquid-Liquid Partitioning

Partition coefficients for several HOCs were either measured or compiled from the literature for a wide range of OILs. An experimental evaluation of a model based on Raoult's law was presented for the partitioning of aromatic hydrocarbons from diesel fuel and coal tar into water, and the results compared to data reported earlier for gasoline/water and motor oil/water partitioning. According to the model based on Raoult's law, the concentration of a constituent in the aqueous phase in equilibrium with an "ideal" organic mixture is proportional to the mole fraction of that constituent in the organic phase. Application of Raoult's law convention for activity coefficients with the assumption of ideal behavior and the use of supercooled liquid solubilities was successful in describing the partitioning of several PAHs within a factor of four for diesel fuels, and within a factor of two for coal tars. UNIFAC (UNIQUE Functional Group Activity Coefficient) model estimates of the likely nonidealities resulting from interactions between components in a simulated gasoline, diesel fuel, motor oil, and coal tar further suggested that the extent of deviations from ideal behavior may be relatively small for these environmentally relevant OILs. Agreement between the model predictions based on Raoult's law and measured liquid-liquid partitioning data is not to be taken as evidence that such compositionally complex organic liquid wastes are indeed ideal mixtures, but rather as support for the pragmatic assumption that ideal behavior might suffice for most practical applications. Thus, first-order estimates of PAH concentrations likely to be found in groundwater (assuming equilibrium) leaving an area contaminated with residual

OILs can be provided with the knowledge of approximate PAH concentrations in the organic phase and the molar volume of the organic phase.

Sorption of Organic Acids

The behavior of organic acids in solvent/water solutions was exceedingly complex. Sorption of organic acids by soils was measured from cosolvent/water solutions as a function of pH and cosolvent fraction (f_c). In methanol/water solutions (0.01 N CaCl_2), decreased sorption compared to that measured in aqueous solutions was observed for the substituted phenols investigated; this finding was similar to that observed for nonpolar organic solutes. Sorption of PCP was adequately characterized by combining the log-linear cosolvency model for predicting cosolvency effects with a model for describing solute speciation effects. For carboxylic acids, the magnitude of sorption observed in methanol/water solutions could not be predicted. Inclusion of cosolvent-induced changes in the solute dissociation constant (pK_a') and the uncertainty of the formation and exchange of charged ion-pairs suggest that deviations from Eq. (3-6) predictions was due to other types of solvent-driven complexation reactions.

To better understand the influence of ionic equilibria on the sorption of organic acids from methanol/water solutions, sorption of benzoic acid by Webster soil was investigated as a function of pH at fixed methanol fractions. Sorption of neutral benzoic acid was observed to decrease with increasing f_c , while benzoate sorption increased. Thus, benzoate is responsible for the enhanced sorption of benzoic acid by soils from methanol/water solutions. Similar trends were not

observed for retention of benzoic acid by RPLC supports in methanol/water solutions buffered with 1:2 stoichiometric mixtures of citrate and phosphate with Na^+ as the counterion. In the latter case, retention of both neutral and ionized benzoic acid, although different in magnitude, decreased with increasing f_c as observed for HOCs.

A preliminary assessment of the data for benzoic acid sorption by several sorbents suggested that the predominant sorbent fraction of interest is still organic matter, as is generally conceptualized to be the case for the sorption of HOCs. Numerous positive correlations have been observed between retention of HOCs by soils and RPLC supports. The lack of such strong correlations between retention by soils and RPLC supports for organic acids reflects the increasing importance of soil functional groups as determinants of HIOC sorption. To explain the enhanced sorption of benzoate by soils, other sorption mechanisms considered were: specific solvent-sorbent and solute-sorbent interactions.

To investigate solvent-sorbent interactions, sorption of benzoic acid in binary mixtures of water and several solvents varying in a wide range of bulk properties was measured. The model based on cosolvent-enhanced solubility and cosolvent-suppressed speciation effects was successful in describing benzoic acid sorption from acetone/water, acetonitrile/water, and 1,4-dioxane/water solutions. Enhanced sorption of benzoic acid from dimethylsulfoxide (DMSO)/water mixtures was similar to that observed from methanol/water solutions; however, the similarities and dissimilarities observed for the different solvent/water systems could not be

attributed to any single bulk solvent property. This suggests that: (1) although both methanol and DMSO have the same macroscopic effect on sorption of benzoic acid, sorption is driven by two completely different mechanisms; or (2) in the presence of water, one of the two solvents acquires a property common to the other solvent. There was spectroscopic evidence found in the literature supporting the formation of $\text{DMSO} \cdot (\text{H}_2\text{O})_2$ complexes and subsequent hydrogen-bonding interactions.

To investigate solute-sorbent interactions, sorption of several substituted carboxylic acids by Webster soil from methanol/water solutions was measured. Comparisons between sorption coefficients observed in neat methanol (K_{MeOH}) and water (K_w), and aqueous ionization constants ($\text{p}K_{\text{a,w}}$) with octanol-water partition coefficients (K_{ow}) for both the ionized (i) and neutral (n) species showed that substantially better correlations were obtained using $K_{\text{ow,i}}$ values. These results further support the dominant role of benzoate in the cosolvent-enhanced sorption of benzoic acid. However, the varied nature of the sorption profiles obtained from the different solvent/water mixtures clearly demonstrates the solvent specificity of this enhancement. In addition, the different trends observed between retention of benzoate by Ca^{+2} -saturated soils versus RPLC supports using mobile phases buffered with monovalent counterions further support the significant role played by various functional groups present in soil organic matter as well as demonstrate the significance of electrolyte composition on sorption of HIOCS. Therefore, enhanced sorption appeared to be a function of specific solvent associations with both the solute and the sorbent. It was deduced that hydrogen-bonding interactions coupled

with selective solvation and preferential orientation of the solvent molecules in the solvation shells about the solute and sorbent are most likely responsible for the enhanced sorption of organic acids by soils in methanol/water and DMSO/water solutions.

Although there remains many uncertainties concerning the specific mechanism responsible for the enhanced sorption of carboxylic acids by soils in mixed solvents, results of this research point to the fallacy of assuming that all organic acids undergo enhanced transport in the presence of an organic cosolvent. This may be directly applied to the assessment of contaminant mobility from a codisposal site, extraction schemes for simultaneous extraction of HIOCs and HOCs, as well as to the expedient design of tracers for alcohol-based fuels (e.g., alternate fuels). In addition, the different sorption profiles observed with various solutes (i.e., HOCs, phenols, carboxylic acids) from solvent/water solutions suggests the use of different solutes to probe solvent-sorbent interactions. Likewise, solute interactions with soil surfaces that are considered negligible in aqueous solutions may become *unmasked* upon addition of a solvent.

Conclusions

- Sorption of organic acids by soils from mixed solvents was solute and solvent dependent.
- Enhanced sorption could not be attributed to a single bulk solvent property.
- Acidity and $K_{ow,i}$ correlated well with K_{MeOH} suggesting the predominant role of benzoate.
- Organic matter is the soil domain of greatest importance.
- Electrolyte composition significantly impacts sorption of carboxylic acids in mixed solvents (i.e., valence).
- Sorption reversible and hysteresis minimal.
- Hydrogen bonding proposed to be a significant mechanism in the enhancement of carboxylic acid sorption in methanol/water and DMSO/water solutions.
- Solute and sorbent heterogeneity (hydrophobic and polar regions), selective solvation, and preferential orientation of solvent molecules were also concluded to be of importance in the sorption of organic acids.

APPENDIX A

SUPERCOOLED LIQUID SOLUBILITIES

The derivation of Eq. (1-1) was based on the pure liquid chemical as the standard state. Many components of interest are crystalline in their pure form at standard state; however, Eq. (1-1) can be extended to solid solutes by employing hypothetical supercooled liquid solubilities (S_{scL}). Super-cooled liquid solubilities cannot be determined directly; however, several estimation methods are available.

Supercooled liquid solubilities of solids can be best understood by examining the steps and reviewing the properties responsible for the solubility of the solid. First, unlike a liquid compound, the crystal structure of the solid must be destroyed forming a super-cooled liquid (A in Figure 1-2). Then, a second step involving the mixing of this hypothetical liquid with the solvent must occur as with a liquid compound (B in Figure 1-2). Thermodynamically, step A involves only the crystallinity properties of the solid (e.g., the heats of fusion and the melting point), whereas the mixing step (B) involves both the properties of the compound and the solvent (e.g., molecular dimensions and interactions). Step A can be interpreted as the hypothetical melting of the compound at the temperature of interest (T) and can be further simplified into three basic steps. The compound is heated from T to its melting temperature (T_m) (Step 1), where it is melted at T_m (Step 2), followed by bringing the compound back to the initial temperature of interest (T) without returning it to the solid (Step 3).

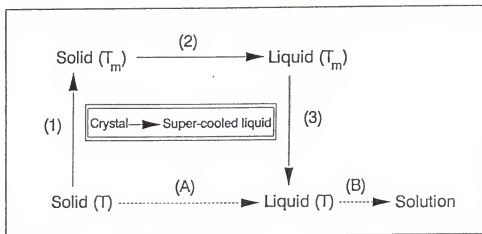


Figure A-1. Schematic representation of the steps involved in the thermodynamic cycle for producing a supercooled liquid from a crystal solute.

Supercooled liquid solubilities (S_{scl}) cannot be determined directly; however, several estimation methods are available. Two of the most widely used methods will be discussed briefly. First, S_{scl} of a compound can be calculated directly from its measured heat of fusion (ΔH_f) and melting point (T_m):

$$\log S_{scl} = \log S_{w,T} + \frac{\Delta H_f}{2.303 R T_m T} (T_m - T) \quad (A-1)$$

where $S_{w,T}$ is the crystal aqueous solubility (moles/L) at a given temperature T (°K); R is the gas constant (kJ/degree mole); ΔH_f is the heat of fusion (Kcal/mole), and T_m is the melting point in °K. For most chemicals of interest, the parameters needed in Eq. (A-1) are available in the literature. Little variation was noted in ΔH_f values for compounds found in more than one literature source; however, in some cases the units reported were in error (e.g., calories vs. joules).

A second estimation method simplifies Eq. (A-1) by assuming that the entropy of fusion ($\Delta H_f/T_m$) (Yalkowsky, 1979; Martin et al., 1979) is the same for all compounds approximately 13.5 cal/mole K yielding the following equation,

$$\log S_{scf} = \log S_w + \frac{2.95 (T_m - T)}{T} \quad (\text{A-2})$$

Eq. (A-2) reduces the number of parameters needed to obtain S_{scf} for a particular compound. Note that when calculating S_{scf} values for a compound at a specific temperature, the corresponding S_w value for that compound at that same temperature must be used. When measured crystal aqueous solubilities are not available at a temperature of interest, various temperature-solubility correlations available in the literature can be used (May, 1980).

APPENDIX B
SAMPLE pK_a DETERMINATION

True thermodynamic ionization constants should be independent of solute concentration. However, the two types of ionization constants typically determined experimentally are concentration ionization constants, better known as "the classical constant" (Albert and Sergeant, 1987), or mixed ionization constants as determined in this study. The *true* thermodynamic constant (K_a^T) must be expressed in terms of activities (a) as follows

$$K_a^T = \frac{a_{H^+} a_{A^-}}{a_{HA}} \quad (B-1)$$

where H^+ , A^- , and HA refer to the hydrogen ion, ionized acid, and neutral acid, respectively. The "classical constant" is written in terms of concentrations as follows

$$K_a^c = \frac{[H^+][A^-]}{[HA]} \quad (B-2)$$

where the brackets ([]) refer to concentrations. The differences between activity- and concentration-based ionization constants principally arise from electrostatic interactions of the ions produced such that some of the ions are not free and active in solution. This results in molar concentrations that are different than the species' activities. These differences become increasingly more significant with increasing

concentrations due to the enhancement of the electrostatic interactions. Hydrogen ion activities were used in combination with concentration-based measurements of the neutral and ionized species of the acid were used to estimate the ionization constant in this study, thus referred to as a "mixed constant".

Titration data for the determination of the mixed ionization constant (K_a^M) for benzoic acid in 10/90 methanol/water solutions are given in Table B-1. Also shown in Tables B-1 and B-2 for each point on the titration curve (pH as a function of base added), are the calculation results for each subsequent steps used to determine K_a^M as given by Albert and Sergeant (1987). Each step is referenced to an equation which is define in Table B-2.

Table B-1. Determination of the ionization constant (pK_a^M) for benzoic acid in 10/90 methanol/water.

V_T (mL)	Meas. pH	$C_{o,T}$ (M)	$C_{HA,T}$ (M)	$C_{A-,T}$ (M)	[HA]/[A ⁻]	pK_a
0.00	3.15	1.00E-02	1.00E-02	0.00E+00		
0.05	3.23	9.98E-03	9.80E-03	1.80E-04	54.43	4.97
0.10	3.29	9.96E-03	9.60E-03	3.60E-04	26.65	4.72
0.15	3.36	9.94E-03	9.40E-03	5.40E-04	17.40	4.60
0.20	3.43	9.92E-03	9.20E-03	7.21E-04	12.77	4.54
0.25	3.49	9.90E-03	9.00E-03	9.01E-04	9.99	4.49
0.30	3.54	9.88E-03	8.80E-03	1.08E-03	8.14	4.45
0.35	3.60	9.86E-03	8.60E-03	1.26E-03	6.81	4.43
0.40	3.65	9.84E-03	8.40E-03	1.44E-03	5.82	4.42
0.45	3.70	9.82E-03	8.20E-03	1.62E-03	5.05	4.40
0.50	3.75	9.80E-03	8.00E-03	1.80E-03	4.43	4.40
0.55	3.79	9.78E-03	7.80E-03	1.98E-03	3.93	4.38
0.60	3.84	9.77E-03	7.60E-03	2.17E-03	3.51	4.39
0.65	3.88	9.75E-03	7.40E-03	2.35E-03	3.15	4.38
0.70	3.92	9.73E-03	7.20E-03	2.53E-03	2.85	4.37
0.75	3.96	9.71E-03	7.00E-03	2.71E-03	2.58	4.37
0.80	3.99	9.69E-03	6.80E-03	2.89E-03	2.35	4.36
0.85	4.03	9.67E-03	6.60E-03	3.07E-03	2.15	4.36
0.90	4.06	9.65E-03	6.40E-03	3.25E-03	1.97	4.35
0.95	4.10	9.63E-03	6.20E-03	3.43E-03	1.81	4.36
1.00	4.13	9.62E-03	6.00E-03	3.62E-03	1.66	4.35
1.05	4.17	9.60E-03	5.80E-03	3.80E-03	1.53	4.35
1.10	4.20	9.58E-03	5.60E-03	3.98E-03	1.41	4.35
1.15	4.24	9.56E-03	5.40E-03	4.16E-03	1.30	4.35
1.20	4.27	9.54E-03	5.20E-03	4.34E-03	1.20	4.35

(Table B-1 continued)

(Table B-1 continued)

V_T (mL)	Meas. pH	$C_{o,T}$ (M)	$C_{HA,T}$ (M)	$C_{A,T}$ (M)	[HA]/[A ⁻]	pK_a^M
1.25	4.30	9.52E-03	5.00E-03	4.52E-03	1.11	4.34
1.30	4.34	9.51E-03	4.80E-03	4.71E-03	1.02	4.35
1.35	4.37	9.49E-03	4.60E-03	4.89E-03	0.94	4.34
1.40	4.40	9.47E-03	4.40E-03	5.07E-03	0.87	4.34
1.45	4.44	9.45E-03	4.20E-03	5.25E-03	0.80	4.34
1.50	4.48	9.43E-03	4.00E-03	5.43E-03	0.74	4.35
1.55	4.51	9.42E-03	3.80E-03	5.62E-03	0.68	4.34
1.60	4.55	9.40E-03	3.60E-03	5.80E-03	0.62	4.34
1.65	4.59	9.38E-03	3.40E-03	5.98E-03	0.57	4.34
1.70	4.63	9.36E-03	3.20E-03	6.16E-03	0.52	4.35
1.75	4.67	9.35E-03	3.00E-03	6.35E-03	0.47	4.34
1.80	4.71	9.33E-03	2.80E-03	6.53E-03	0.43	4.34
1.85	4.76	9.31E-03	2.60E-03	6.71E-03	0.39	4.35
1.90	4.81	9.29E-03	2.40E-03	6.89E-03	0.35	4.35
1.95	4.86	9.28E-03	2.20E-03	7.08E-03	0.31	4.35
2.00	4.91	9.26E-03	2.00E-03	7.26E-03	0.28	4.35
2.05	4.97	9.24E-03	1.80E-03	7.44E-03	0.24	4.35
Average $pK_a^M = 4.37$						

To correct for the effect of the solvent on the e.m.f. measurements, pH measurements of 0.001 M HCl aqueous solution was compared to the 0.001 M HCl in the appropriate mixed solvent. The difference was added to the average pK_a^M value estimated from the titration. Each titration set was performed in triplicate and the estimated pK_a^M values averaged. For the titration exemplified above, there was no difference between the measured pH values of the 0.001 M HCl aqueous and mixed solvent solution (pH = 3.07).

Table B-2. Parameters and equations for calculating results in Table B-1.

$$H^+ = 10^{(m \cdot pH - b)} \quad (B-3)$$

$$C_{o,T} = C_i \frac{V_i}{V_i + V_T} \quad (B-4)$$

$$C_{HA,T} = C_i - (V_T C_T) \quad (B-5)$$

$$C_{A^-,T} = C_i - C_{HA,T} \quad (B-6)$$

$$pK_a^M = \frac{[A^-] a_{H^+}}{[HA]} \quad (B-7)$$

where

C_i = Initial benzoic acid concentration (0.01 M)

C_T = Titer concentration (0.01 M NaOH)

V_i = Initial Volume (25 mL)

V_T = volume of titer added (mL 0.01 M NaOH)

pH meter coefficients used to calculate pH from e.m.f:

m = slope = -1

b = intercept = 6.86E-06

subscripts:

T refers to at a given point (V_T, pH) on the titration curve

HA refers to neutral species of the organic acid

A^- refers to ionized species of the organic acid

REFERENCES

- Abrams, D.S. and J.M. Prausnitz. 1975. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs' energy of partly or completely miscible systems. *Am. Inst. Chem. Eng. J.*, 21:116-128.
- Ainsworth, C.C., J.M. Zachara, and R.L. Schmidt. 1987. Quinoline sorption on Na-montmorillonite: Contributions of the protonated and neutral species. *Clays and Clay Minerals*, 35: 121-128.
- Albert, A. and E.P. Sergeant. 1984. Determination of Ionization Constants: A Laboratory Manual, 3rd ed.; Chapman and Hall, Ltd., London.
- Almeida Macedo, E., U. Weidlich, J. Gmehling, and P.A. Rasmussen. 1983. Vapor-liquid equilibria by UNIFAC Group Contribution. Revision and Extension. 3, *Ind. Eng. Chem. Process Des. Dev.*, 22:676-678.
- Augustijn, D.C.M., R.E. Jessup, P.S.C. Rao, and A.L. Wood. 1992. Remediation of contaminated soils by solvent flushing. *J. Environ. Eng.* (in review).
- Arbuckle, W.B. 1986. Using UNIFAC to calculate aqueous solubilities. *Environ. Sci. Technol.*, 20:1060-1064.
- Bacarella, A.L., E. Grunwald, H.P. Marshall, and E.L. Purlee. 1955. The potentiometric measurement of acid dissociation constants and pH in the system methanol/water. *Potentiometric Meas.*, 20:747-763.
- Bailey, G.W., J.L. Qhite, and T. Rothberg. 1968. Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. *Soil Sci. Soc. Amer. Proc.*, 32:222-234.
- Bakhtar, D., G.R. Bradford, and L.J. Lund. 1989. Dissolution of soils and geological materials for simultaneous elemental analysis by inductively coupled plasma optical-emission spectrometry and atomic-adsorption spectrometry. *Analyst*, 114(8):901-999.
- Ball, W.P., C.H. Buehler, T.C. Harmon, D.M. Mackay, and P.V. Roberts. 1990. Characterization of a sandy aquifer material at the grain scale. *J. Contam. Hydrol.*, 5:253-295.

- Ball, W.P. and P.V. Roberts. 1991a. Long-term sorption of halogenated organic chemicals by aquifer material. 1. Equilibrium. *Environ. Sci. Tech.*, 25:1223-1237.
- Ball, W.P. and P.V. Roberts. 1991b. Long-term sorption of halogenated organic chemicals by aquifer material. 2. Intraparticle diffusion. *Environ. Sci. Tech.* 25:1237-1249.
- Banerjee, S. 1984. Solubilities of organic mixtures in water. *Environ. Sci. Tech.*, 18:587-591.
- Bates, R.G. 1973. pKa values for carboxylic acids and anilinium ions. Determination of pH, Theory and Practice, 2nd ed.; Wiley, New York. p 452.
- Bates, R.G., 1963. Interpretation of pH measurements in alcohol-water solvents. *J. Phys. Chem.*, 67:1833.
- Bellin, C. A. 1993. Ph.D. Dissertation. Coupled-Processes: Interactions of Contaminants, Bacteria, and Surfaces. University of Florida, Gainesville, FL.
- Bourguignon, B., F. Marcenac, H.R. Keller, P.F. de Qguiar, and D.L. Massart. 1993. Simultaneous optimization of pH and organic modifier content of the mobile phase for the separation of chlorophenols using a Doehlert design. *J. Chromatog.*, 628:171-189.
- Brenner, H. 1962. The diffusion model of longitudinal mixing in beds of finite length. Numerical Values. *Chem. Eng. Sci.*, 17:229.
- Briggs, G.G. 1981. Theoretical and experimental relationships between soil adsorption, octanol/water partition coefficients, water solubilities, bioconcentration factors, and the parachor. *J. Agric. Food Chem.*, 29:1050.
- Brown, D.S. and G. Combs. 1985. A modified Langmuir equation for predicting sorption of methylacridinium in soils and sediments. *J. Environ. Qual.*, 14:195-199.
- Brusseau, M.L., R.E. Jessup, and P.S.C. Rao. 1990. Sorption kinetics of organic chemicals: Evaluation of gas-purge and miscible-displacement techniques. *Environ. Sci. Tech.*, 24:727-735.

- Callahan, M.A., M.W. Slimak, N.W. Gabel, I.P. May, C. Fowler, J.R. Freed, P. Jennings, R.L. Durfee, F.C. Whitmore, B. Maestri, M.W. Mabey, B.R. Holt, and C. Gould. 1979. Water-related environmental fate of 129 priority pollutants. USEPA, Washington, DC. Vol. I and II, EPA-440/4-79-029a and EPA-440/4-79-029b.
- Chen, C. S-H. 1993. Partitioning of Motor Oil Components into Water. Master's Thesis, University of Florida, Gainesville, FL.
- Chiou, C.T., L.S. Peters, and V.H. Freed. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. *Sci.*, 206:831-832.
- Chiou, C.T., P.E. Porter, and D.W. Schmedding. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environ. Sci. Tech.*, 17: 227-231.
- Chiou, C.T. and D.W. Schmedding. 1982. Partitioning of organic compounds in octanol-water systems. *Environ. Sci. Tech.*, 16:4-10.
- Choi, P.B., C.P. Williams, K.G. Buehring, and E. McLaughlin. 1985. Solubility of aromatic hydrocarbons in mixtures of benzene and cyclohexane. *J. Chem Eng. Data*, 30:403-409.
- Cline, P.V., J.J. Delfino, and P.S.C. Rao. 1991. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures. *Environ. Sci. Tech.*, 25:914-920.
- Davis, J.A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochimica et Cosmochimica Acta*, 46:2381-2393.
- Dean, J.A. 1985. *Lange's Handbook of Chemistry*, 13th ed. McGraw-Hill Inc., New York, NY.
- De Ligny, C.L. and M. Rehbach. 1960. The liquid-junction potentials between some buffer solutions in methanol and methanol-water mixtures and a saturated KCl solution in water at 25°C. *Recueil*, pp.727-730.
- Dzombak, D.A. and R.G. Luthy. 1984. Estimating sorption of polycyclic aromatic hydrocarbons on soils. *Soil Sci.*, 137:292-308.
- Eisenberg, D. and W. Kauzmann. 1969. *The Structure and Properties of Water*. Oxford University Press, New York.

- Eng, R. and M. Menzies. 1985. Survey of town gas and by-product production and location in the United States (1880-1950), PB-8 J 1738B. National Technical Information Service, Washington, DC.
- EPRI. 1989. MYGRT™ code version 2.0: An IBM code for simulating migration of organic and inorganic chemicals in Groundwater. Report EN-6531. EPRI, Washington, DC.
- EPRI. 1993. Chemical and physical characteristics of coal tar from selected manufactured gas plant (MGP) sites. EPRI-RP2879-01,12 EPRI, Washington, DC (In press).
- Farmer, V.C. and J.D. Russell. 1967. IN: Fifteenth Conference of Clays and Clay Minerals, pp. 121-142.
- Felice, L.J., J.M. Zachara, R.L. Schmidt, and R.T. Resch. 1985. Quinoline partitioning in subsurface materials: Adsorption, desorption and solute competition. IN: Proc. 2nd Internl. Conf. on Groundwater Quality Research. N.N. Durham and A.E. Redelfs (Eds.) Tulsa, OK. pp. 39-41.
- Fontaine, D.D., R.G. Lehmann, and J.R. Miller. 1991. Soil adsorption of neutral and anionic forms of a sulfonamide herbicide, flumetsulam. J. Envir. Qual., 20(4):759-762.
- Franks, F. and D.G. Ives. 1966. The structural properties of alcohol-water mixtures. Quarterly Reviews, 20:1-45.
- Fredenslund, A., R. Jones, and J.M. Prausnitz. 1975. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. Amer. Inst. Chem. Eng. J., 21:1086-1099.
- Freeman, D.H. and L.W. Cheung. 1981. A gel-partition model for organic desorption from a pond sediment. Sci., 214:790.
- Fu, J.K. and R.G. Luthy. 1986a. Aromatic compound solubility in solvent/water mixtures. J. Envir. Eng., 112:328-345.
- Fu, J.K. and R.G. Luthy. 1986b. Effect of organic solvent on sorption of aromatic solutes onto soils. J. Envir. Eng., 112:346-366.
- Gehron, M.J. 1988. Advanced Mass Spectrometric Methods of Jet Fuel Analysis, Ph.D. Dissertation. University of Florida, Gainesville, FL.

- Gelsemsa, W.J., C.L. De Ligny, A.G. Remijnse and Miss H.A. Blijleven. 1967. pH-measurements in alcohol-water mixtures, using aqueous standard buffer solutions for calibration. *Recueil*, pp. 647-660.
- Gerstl, Z. 1990. Estimation of organic chemical sorption by soils. *J. Contam. Hydrol.*, 6:357-375.
- Gmehling, J., P.A. Rasmussen, and A. Fredenslund. 1982. Vapor-liquid equilibria by UNIFAC group contribution. Revision and extension. 2, *Ind. Eng. Chem. Process Des. Dev.*, 21:118-127.
- Goldwasser, J.M., A. Rudin, and W.L. Eldson. 1982. Characterization of copolymers and polymer mixtures by gel permeation chromatography. *J. Liq. Chromat.*, 5:2253-2257.
- Green, R.E. and S.W. Karickhoff. 1990. Sorption estimates for modeling. IN: *Pesticides in the soil environment*. H.H. Cheng (Ed.). Soil Sci. Soc. Amer., Inc., Madison, WI. pp. 70-102.
- Groher, D.M. 1990. An Investigation of factors affecting the concentrations of polyaromatic hydrocarbons in groundwater at coal tar waste sites. Master's Thesis, Massachusetts Institute of Technology, Boston, MA.
- Grover, R. and Smith, A. E. 1974. Adsorption studies with acid and dimethylamine forms of 2,4-D and dicamba. *Can. J. Soil* 54:179-186.
- Guerin, M.R. 1978. Energy sources of polycyclic aromatic hydrocarbons. IN: *Polycyclic Hydrocarbons and Cancer*. H.V. Gelboin and P.O.P. Tso (Eds.). Academic Press, New York, Vol I., pp 3-42.
- Hagwall, M. 1992. Partitioning of aromatic constituents into water from diesel fuel. Master's Thesis, The Royal Institute of Technology, Stockholm, Sweden.
- Hansen, H.K., P. Rasmussen, and A. Fredenslund. 1991. Decomposition of dichlorodifluoromethane on BPO_4 . *Ind. Eng. Chem. Res.*, 30:2355.
- Harned, H.S. and B.B. Owen. 1958. *The Physical Chemistry of Electrolyte Solutions*. Amer. Chem. Soc., Washington DC.
- Hassett, J.J., W.L. Banwart, S.G. Wood, and J.C. Means. 1981. Sorption of α -naphthol: Implications concerning the limits of hydrophobic sorption. *Soil Sci. Soc. Amer. J.*, 45:38-42.

- Hesleitner, P., N. Kallay, and E. Matijevic. 1991. Adsorption of solid/liquid interfaces. 6. The effect of methanol and ethanol on the ionic equilibria at the hematite/water interface. *Langmuir*, 7:178-184.
- Hess, R.E. and R.A. Plane. 1964. A raman spectrophotometric comparison of interionic association in aqueous solutions of metal nitrates, sulfates, and perchlorates. *Inorg. Chem.*, 3:769-770.
- Hingston, F.J. 1981. A review of anion adsorption. IN: Adsorption of Inorganics at the Solid-Liquid Interface. M.A. Anderson and A.J. Rubin. (Eds.). Ann Arbor Sci., Ann Arbor, MI.
- Horvath, C. 1973. High performance ion-exchange chromatography with narrow-bore columns: rapid analysis of nucleic acid constituents at the subnanomole level. *Methods Biochem. Anal.*, 21:79-154.
- Horvath, D., W. Melander, and I. Molnar. 1976. Solvophobic interactions in liquid-chromatography with nonpolar stationary phases. *J. Chromat.*, 125(1):129-156.
- Horvath, C., W. Melander, and I. Molnar. 1977. Liquid chromatography of ionogenic substances with nonpolar stationary phases. *Anal. Chem.*, 49:142-154.
- Humburg, N.E., E.R. Hill, L.M. Kitchen, S.R. Colby, R.G. Lynn, W.J. McAvoy, and R. Prasad. *Herbicide Handbook of the Weed Science Society of America*, 6th ed. Weed Sci. Soc. Amer., Champaign, IL.
- IFAS, 1974 University of Florida, Institute of Food and Agricultural Sciences. Characterization Data for Selected Florida Soils, Soil Science Research Report 74-1.
- Jafvert, C.T. 1990. Sorption of organic acid compounds to sediments: Initial model development. *Envir. Toxic. and Chem.*, 9:1259-1268.
- Jandera, P. and J. Churacek. 1973. Ion exchange chromatography of carboxylic acids. *J. Chromat.*, 86:351-421.
- Johnson, C.A. and J.C. Westall. 1990. Effect of pH and KCl Concentration on the Octanol-water Distribution of Methylanilines. *Envir. Sci. Tech.*, 24:869-875.

- Johnson, R.L., S.M. Brillante, L.M. Isabelle, J.E. Houck, and J.F. Pankow. 1985. Migration of chlorophenolic compounds at the chemical waste disposal site at Alkali Lake, Oregon. 2. Contaminant distributions, transport, and retardation. *Groundwater*, 23:652-666.
- Kaiser, K.L.E. and I. Valdmanis. 1982. Apparent octanol/water partition coefficients of pentachlorophenol as a function of pH. *Can. J. Chem.*, 60:2104-2106.
- Kan, A.T. and M.B. Tomson. 1990. Effect of pH and concentration on the transport of naphthalene in saturated aquifer media. *J. Contam. Hydrol.*, 5:235-251.
- Karger, Barry L., James N. LePage, and Nobuo Tanaka. 1980. Secondary chemical equilibria in high-performance liquid chromatography. IN: *High Performance Liquid Chromatography. Advances and Perspectives*. C. Horvath (Ed.). Academic Press, Inc., New York, Vol. 1, pp.128-131.
- Karickhoff, S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, 10:833-846.
- Karickhoff, S.W. 1984. Organic pollutant sorption in aquatic systems. *J. Hydraulic Eng.*, 110:707-735.
- Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Research*, 13:241-248.
- Kearney, P.C. and D.D. Kaufman, 1976. *Degradation and Mode of Action: Volume 2*, Marcel Dekker Inc., New York.
- Kenaga, E.E. and C.A.I. Goring. 1980. Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota. IN: *Aquatic Toxicology*. J.G. Eaton, P.R. Parrish, and A.C. Hendricks (Eds.) Special Technical Publication 707; American Society for Testing of Materials: Philadelphia, PA, pp. 78-115.
- Kirk-Othmer Encyclopedia of Chemical Technology. 1980. 3rd ed.; John Wiley & Sons; New York. Vol. 11.
- Kohl, R.A. and S.A. Taylor. 1961. Hydrogen bonding between the carbonyl group and Wyoming bentonite. *Soil Sci.*, 91:223-227.

- Koskinen, W.C., and S.S. Harper. 1990. The retention process: mechanisms. IN: Pesticides in the Soil Environment: Processes, Impacts and Modeling, Soil Sci. Soc. of Am. Book Series 2. pp. 51-78.
- Koskinen, W.C., G.A. O'Connor, and H.H. Cheng. 1979. Characterization of hysteresis in the desorption of 2,4,5-T from soils. Soil Sci. Soc. Am. J., 43:871-874.
- Kukowski, H. 1989. Untersuchungen zur ad- und desorption ausgewählter chemikalien in böden. Ph.D. Dissertaion. University of Kiel, Kiel, Germany.
- Kummert, R. and W.J. Stumm. 1980. The surface complexation of organic acids on hydrous- Al_2O_3 . Colloid and Interface Sci., 75:373-385.
- Lambert, S.M. 1967. Functional relationship between sorption in soil and chemical structure. J. Agri. Food Chem., 15:572-576.
- Lane, B.F. and R.C. Loehr. 1992. Estimating the equilibrium aqueous concentrations of polynuclear aromatic hydrocarbons in complex mixtures. Envir. Sci. Tech., 26:983-990.
- Lee, L.S., C.A. Bellin, R. Pinal, and P.S.C. Rao. 1993a. Cosolvent effects on sorption of organic acids by soils from mixed-solvents. Envir. Sci. Tech., 27:165-171.
- Lee, L.S., P.S.C. Rao, and M.L. Brusseau. 1991. Nonequilibrium sorption and transport of neutral and ionized chlorophenols. Envir. Sci. Tech., 25: 722-729.
- Lee, L.S., P.S.C. Rao, M.L. Brusseau, and R.A. Ogwada. 1988. Nonequilibrium sorption of organic contaminants during flow through columns of aquifer materials. Envir. Toxicol. and Chem., 7:779-793.
- Lee, L.S., P.S.C. Rao, P. Nkedi-Kizza, and J.J. Delfino. 1990. Influence of solvent and sorbent characteristics on distribution of pentachlorophenol in octanol-water and soil-water systems. Envir. Sci. Tech., 24:654-661.
- Leo, A., C. Hansch, and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev., 71:525-553.
- Lewis, S. and I.D. Wilson. 1984. Factors affecting the ion-pair reversed-phase thin-layer chromatography of organic acids on paraffin-coated and C18 bonded silica gel. J. Chromat., 312:133-140.

- Little, Arthur D. 1981. Reference constants for priority pollutants and selected chemicals. Reference #84204. Report to Wald, Harkrader, and Ross. Washington, DC.
- Loeppert Jr., R.H., L.W. Zelany, and B.G. Volk. 1977. Acidic properties of kaolinite in water and acetonitrile. *Soil Sci. Soc. Am. J.*, 41:1101-1106.
- Loeppert Jr., R.H., L.W. Zelany, and B.G. Volk. 1979. Titration of pH-dependent sites of kaolinite in water and selected nonaqueous solvents. *Clays and Clay Minerals*, 27: 57-62.
- Loeppert Jr., R.H., L.W. Zelany, and B.G. Volk. 1986. Acid properties of montmorillonite in selected solvents. *Clays and Clay Minerals*, 34:87-92.
- Ludwig, M., V. Baron, K. Kalfus, O. Pytela, and M. Vecera. 1986. Dissociation constants of substituted benzoic acids in water and in organic solvents. *Collection Czechoslovak Chem. Commun.*, 51:2135-2142.
- Luthy, R.G., D.A. Dzombak, C.A. Peters, M.A. Ali, and S.B. Roy. 1993. In situ solvent extraction for remediation of coal tar sites. Technical Report, Carnegie Mellon University, Pittsburgh, PA (in press).
- MacIntyre, W.G. and P.O. deFur. 1985. The effect of hydrocarbon mixtures on adsorption of substituted naphthalenes by clay and sediment from water. *Chemosphere*, 14(1):103-111.
- MacKay, D., W.Y. Shui, A. Chau, J. Southwood, and C.I. Johnson. 1985. Environmental fate of diesel fuel spills on land. Report for Assoc. of Amer. Railroads, Dept. Chem. Eng. and Applied Chem., University of Toronto.
- Mangnussen, T., P. Rasmussen, and A. Fredenslund. 1981. UNIFAC parameter table for prediction of liquid-liquid equilibria. *Ind. Eng. Chem. Process Des. Dev.*, 20:331-334.
- Marcus, Y. 1984. The effectivity of solvents as electron pair donors. *J. Solution Chem.*, 13:599-624.
- Marques, R.M.L. and P.J. Schoenmakers. 1992. Modeling retention in reversed-phase liquid-chromatography as a function of pH and solvent composition. *J. Chromat.*, 592(1-2):157-182.
- Martin, E., S.H. Yalkowsky, and J.E. Wells. 1979. Fusion of disubstituted benzenes. *J. Pharm. Sci.*, 68:565-568.

- May, W.E. 1980. "The solubility behavior of polycyclic aromatic hydrocarbons in aqueous systems". IN: *Petroleum in the Marine Environment*. L. Petrakis and F.T. Weiss (Eds.). American Chemical Society, Washington DC, Adv. Chem. Series, No. 185, pp. 143-192.
- McGinnis, G.D., H. Borazjani, L.K. McFarland, D.F. Pope, and D.A. Strobel. 1989. Characterization and laboratory soil treatability studies for creosote and pentachlorophenol sludges and contaminated soil. EPA/600/S2-88/055. U.S. EPA, Ada, OK.
- Miller, M.M., P. Wasik, G.-L. Huang, W.-Y. Shiu, and D. Mackay. 1985. Relationships between octanol-water partition coefficients and aqueous solubility. *Envir. Sci. Tech.*, 19:522-529.
- Millner, G.C., R.C. James, and A.C. Nye. 1992. Human health-based soil cleanup guidelines for diesel fuel No. 2. *J. Soil Contam.*, 1:103-157.
- Mingelgrin, U. and Z. Gerstl. 1983. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. *J. Envir. Qual.*, 12:1-11.
- Morris, K.R., R. Abramowitz, R. Pinal, P. Davis, T. S. Kowsky. 1988. Solubility of aromatic pollutants in mixed solvents. *Chemosphere*, 17:285-298.
- Mrkvičáková, L. and S. Pokorný. 1985. On the reliability of molecular weight determination by vapor phase osmometry. *J. Appl. Polymer Sci.*, 30:1211-1218.
- Murray, M.R. and J.K. Hall. 1989. Sorption-desorption of dicamba and 3,6-dichlorosalicylic acid in soils. *J. Envir. Qual.* 18(1):51-57.
- Nelson, D.W. and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. IN: *Methods of Soil Analysis, Part 2-Chemical and Microbiological Properties*, 2nd ed. A.L. Page, R.H. Miller, R.H., and D.R. Keeney (Eds.). ASA and SSSA Publ., Madison, WI, Ch. 29, pp. 570-573.
- Nicholls, P. H. and A. A. Evans. 1991. Sorption of ionisable organic compounds by field soils. Part 2: Cations, bases, and zwitterions. *Pesticide Sci.*, 33:331-345.
- Nkedi-Kizza, P., M.L. Brusseau, P.S.C. Rao, and A.G. Hornsby. 1989. Sorption nonequilibrium during displacement of hydrophobic organic chemicals and ⁴⁵Ca through soil columns with aqueous and mixed solvents. *Envir. Sci. Tech.*, 23:814-820.

- Nkedi-Kizza, P., P.S.C.Rao, and A.G. Hornsby. 1985. Influence of organic cosolvent on sorption of hydrophobic organic chemicals by soils. *Envir. Sci. Tech.*, 19:975-979.
- Nkedi-Kizza, P., P.S.C.Rao, and A.G. Hornsby. 1987. The influence of organic cosolvents on leaching of hydrophobic organic chemicals through soils. *Envir. Sci. Tech.*, 21:1107-1111.
- O'Connor, J.T., M.M. Ghosh, S.K. Banerji, K. Piontek, E. Aguado, and T.M. Prakash. 1989. Organic groundwater contamination evaluation and prediction (in review).
- Okuda, I., L.S. Lee, and P.S.C.Rao. 1991. Dissolution and desorption of polyaromatic hydrocarbons from nonaqueous phase liquid wastes. IN: American Chemical Society, Division of Environmental Chemistry, Preprints of Papers Presented at the 201st National Meeting, Atlanta, GA. April 14-19, Vol. 31, No. 1:467-469.
- Ou, L.T., D.F. Rothwell, and M.V. Mesa. 1985. Soil sterilization by 2450 MHz microwave radiation. *Soil Crop Sci. Soc. Fla. Proc.*, 44:77-80.
- Pal, A., S.K. Maity, and S.C. Lahari. 1983. Free energies of transfer of ions from solubility and conductometric measurements. *J. Indian Chem. Soc.*, LX:640-642.
- Palmer, C.D. and W. Fish. 1992. Chemical Enhancements to Pump-and-treat Remediation. Ground Water Issue. EPA/540/S-92/001. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC.
- Parks, G.A.. 1967. Aqueous surface chemistry of oxides and complex oxide minerals. Isoelectric point and zero point of charge. IN: *Equilibrium Concepts in Natural Water Systems*. Adv. in Chem. Series no. 67. W. Stumm (Ed.). American Chemical Society, Washington, DC, pp. 94-103.
- Patterson, R.J. and H.M. Liebscher. 1987. Laboratory simulation of pentachlorophenol/ phenate behavior in an alluvial aquifer. *Water Pollut. Res. J. Canada*, 22:147-155.
- Perrin, D.D., B. Dempsey and E.P. Serjeant. 1981. pK_a Prediction for Organic Acids and Bases. Chapman and Hall Ltd., London, Great Britain.

- Perrin, D.D. 1965. Dissociation Constants of Organic Bases in Aqueous Solution. Butterworths, London.
- Perrin, E.E. 1972 supplement. Dissociation Constants of Organic Bases in Aqueous Solution. Butterworths, London.
- Peters, C.A. 1992. Experimental evaluation and semi-empirical thermodynamic modeling of coal tar dissolution in water-miscible solvents. Ph.D. Dissertation, Carnegie Mellon, Pittsburgh.
- Peters, R.A. 1931. Interfacial tension and hydrogen-ion concentration. Proc. Roy. Soc. (London), A133:140-154.
- Picel, K.C., V.C. Stamoudis, and M.S. Simmons. 1988. Distribution coefficients for chemical components of a coal-oil/water system. Water Res., 22:1189-1199.
- Pinal, R. 1988. Estimation of Aqueous Solubility of Organic Compounds, Ph.D. Dissertation, Univ. of Arizona, Tucson, AZ.
- Pinal, R., L.S. Lee, and P.S.C. Rao. 1991. Prediction of the solubility of hydrophobic compounds on nonideal solvent mixtures. Chemosphere, 22:939-951.
- Pinal, R., P.S.C. Rao, L.S. Lee, and P.V. Cline. 1990. Cosolvency of partially-miscible organic solvents on the solubility of hydrophobic organic chemicals. Envir. Sci. Tech., 24:639-647.
- Popovych, O. and R.P.T. Tomkins. (1981) Nonaqueous Solution Chemistry. ohn Wiley and Sons New York.
- Prausnitz, J.M., T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh, and J.P. O'Connell. 1980. Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria, rentice-Hall, Inc. Englewood Cliffs, N.J.
- Rao, P.S.C., A.G. Hornsby, D.P. Kilcrease, and P. Nkedi-Kizza. 1985. Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation. J. Envir. Qual., 14:376-383.

- Rao, P.S.C. and R.E. Jessup. 1983. Sorption and movement of pesticides and other toxic substances in soils. IN: Chemical Mobility and Reactivity in Soil Systems. D.W. Nelson, K.K. Tanji. and D.E. Elrick (Eds.). American Society of Agronomy and Soil Science Society of American Special Publication No. 11. American Society of Agronomy, Madison, WI, pp. 183-201.
- Rao, P.S.C., and L.S. Lee. 1988. Sorption of organic chemicals by soils from multi-solvent and multi-sorbate mixtures. IN: Health and Environmental Research on Complex Organic Mixtures. R.H. Gray, E.K. Chess, P.J. Mellinger, R.G. Riley, and D.L. Springer (Eds.). DOE 62 Symposium Series. 24th Hanford Life Sciences Symposium, Battelle, Washington. pp. 457-471.
- Rao, P.S.C., L.S. Lee, P. Nkedi-Kizza, and S.H. Yalkowsky. 1989. Sorption and transport of organic pollutants at waste disposal sites. IN: Toxic Organic Chemicals in Porous Media. Z. Gerstl, Y. Chen, U. Mingelgrin, and B. Yaron (Eds.) Springer-Verlag, Berlin, Germany. pp. 176-192.
- Rao, P.S.C., L.S. Lee, and R. Pinal. 1990. Cosolvency and sorption of hydrophobic Organic chemicals. *Envir. Sci. Tech.*, 24:647-654.
- Rao, P.S.C. and P. Nkedi-Kizza (Eds.). 1987. Development and testing of protocol for selecting the principal hazardous constituents (PHCs in a waste stream). Progress Completion Report, CR# 811035. U.S. Environmental Protection Agency.
- Rao, P.S.C., P. Nkedi-Kizza, and J.M. Davidson. 1986. IN: Land Treatment: A Hazardous Waste Management Alternative, Water Research Symp. Series 13, Austin, TX. pp. 63-72.
- Rao, P.S.C., R. D. Rhue, C.T. Johnston, and R.A. Ogwada. 1988. Sorption of Selected Volatile Organic Constituents of Jet Fuels and Solvents on Natural Sorbents from Gas- and Solution-Phases. Project Completion Report, ESL-TR-02. U.S. Air Force.
- Rhue, R. D. and W.H. Reve. 1990. Exchange capacity and adsorbed-cation charge as affected by chloride and perchlorate. *Soil Sci. Soc. Amer. J.*, 54:705-708.
- Reichardt, K. 1990. Soil spacial variability and symbiotic nitrogen fixation by legumes. *Soil Sci.*, 150(3):579-587.
- Reick, C.E. and R.D. Carringer. 1977. Effect of n,n-diallyl dichloroacetamide on EPTC degradation. *ABS PAP ACS*, 173(Mar20):71.

- Rostad, C.E., W.E. Pereira, and M.F. Hult. 1985. Partitioning studies of coal-tar constituents in a two phase contaminated ground-water system. *Chemosphere*, 14:1023-1036.
- Rubino, J. 1988. Electrostatic and non-electrostatic free energy contributions to acid dissociation constants in cosolvent-water mixtures. *International J. Pharmaceutics*, 42:181-191.
- Rubino, J. T. and J.T. Berryhill. 1986. Effects of solvent polarity on the acid dissociation constants of benzoic acids. *J. Pharm. Sci.*, 75:182-186.
- Rubino, J.T., J. Blanchard, and S.H. Yalkowsky. 1984. Solubilization by cosolvents II: Phenytoin in binary and ternary solvents. *J. Parenteral Sci. & Tech.*, 38:215-221.
- Rubino, J.T. and S.H. Yalkowsky. 1985. Solubilization by cosolvents III: Diazepam and benzocaine in binary solvents. *J. Parenteral Sci. & Tech.*, 39:106-111.
- Rubino, J.T. and S.H. Yalkowsky. 1987a. Cosolvency and cosolvent polarity. *Pharm. Res.*, 4:220-230.
- Rubino, J.T. and S.H. Yalkowsky. 1987b. Cosolvency and deviations from log-linear behavior. *Pharm. Res.*, 4:231-236.
- Rubino, J.T. and S.H. Yalkowsky. 1987c. Solubilization by cosolvents IV: Benzocaine, diazepam and phenytoin in aprotic solvent-water mixtures. *J. Parenteral Sci. & Tech.*, 41:172-176.
- Sabljić, A. 1984. Predictions of the nature and strength of soil sorption of organic pollutants by molecular topology. *J. Agric. Food Chem.*, 32:243-246.
- Sabljić, A. 1987. On the prediction of soil sorption coefficients of organic pollutants from molecular structure: Applications of a molecular topology model. *Envir. Sci. Tech.*, 21:358-366.
- Sanemasa, I., Y. Miyazaki, S. Arakawa, M. Kumamaru, and T. Deguchi. 1987. The solubility of benzene-hydrocarbon binary-mixtures in water. *Bull. Chem. Soc. Jpn.*, 60(2):517-523.
- Sangster, J. 1989. Octanol-water partition coefficients of simple organic compounds. *Phys. and Chem. Ref. Data.*, 18:1111.

- Schellenberg, K., C. Leunberger, and R.P. Schwarzenbach. 1984. Sorption of chlorinated phenols by natural sediments and aquifer materials. *Envir. Sci. Tech.*, 18:652-657.
- Schneider, V.H. and H. Strehlow. 1962. Über auswählende solvation von ionen in lösungsmittelgemischen. II, *Z. Phys. Chem. (Frankfurt)*, 49:309-314.
- Schoenmakers, Peter J., Sylvie van Molle, Carmel M.G. Hayes and Louis G.M. Uunk. 1991. Effects of pH in reversed-phase liquid chromatography. *Analytica Chimica Acta*, 250:1-19.
- Schwarzenbach, R.P. and J.C. Westall. 1981. Transport of nonpolar organic compounds from surface water to groundwater: Laboratory sorption studies. *Envir. Sci. Tech.*, 15:1360-1367.
- Schwarzenbach, R.P. and J.C. Westall. 1985. Sorption of hydrophobic trace organic compounds in groundwater systems. *Water Sci. Tech.*, 17:39-55.
- Seip, H. M., J. Alstad, G. E. Carlberg, K. Martinsen, and R. Skaane. 1986. Measurement of mobility of organic compounds in soil. *The Sci. Total Envir.*, 50:87-101.
- Sergeant, E.P. and B. Dempsey. 1979. *Ionisation Constants of Organic Acids in Aqueous Solution*. Pergamon Press, Oxford.
- Shoemaker, D.P., C.W. Garland, J.I. Steinfeld, and J.W. Nibler. 1980. *Experiments in Physical Chemistry*, 4th ed. McGraw-Hill Book Co. New York.
- Shorten, C.V. and A.W. Elzerman. 1989. Desorption of phenanthrene in coal contaminated sediments: Effect of organic cosolvents on release kinetics. *Envir. Sci. Tech. (In Review)*.
- Skjold, S., B. Kolbe, J. Gmehling, and P. Ramussen. 1979. Vapor-liquid equilibria by UNIFAC group contribution. Revision and extension. *Ind. Eng. Chem. Process Des. Den. Sci. Technol.*, 19:522-529.
- Soerens, Thomas S. and David A. Sabatini. 1992. Cosolvency effects on sorption of Rhodamine WT. IN: *Tracer Hydrology*, 131-134.
- Sposito, G. 1981. The operational definition of the zero point of charge in soils. *Soil Sci. Soc. Am. J.*, 45:292-297.

- Sposito, G. 1984. *The Surface Chemistry of Soils*. Oxford University Press, New York, pp. 78-88.
- Sposito, G. 1989. *The Chemistry of Soils*. Oxford University Press, New York.
- Stauffer, T.B. 1988. Sorption of nonpolar organics on minerals and aquifer materials. Ph.D. Dissertation., School of Marine Sciences, The College of William and Mary, VA.
- Stephen, H., and T. Stephen. 1963. *Solubilities of Inorganic and Organic Compounds*. Vol. 1, Binary Systems, Part 1. Pergamon Press, Macmillan Co., New York.
- Strehlow, H. and H.M. Koepp. 1958. Über auswählende solvation von ionen in lösungsmittelgemischen. *Z. Elektrochem.* 62(3):373-378.
- Stumm, W., R. Kummert, and L. Sigg. 1980. A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. *Croatica Chemica Acta*, 53: 291-312.
- Swarc, M. 1974. *Ions and Ion Pairs in Organic Reactions*. Volume 2; John Wiley and Sons; New York.
- Thomas, D.H. and J.J. Delfino. 1991. A gas chromatographic/chemical indicator approach to assessing ground water contamination by petroleum products. *Ground Water Monitoring Rev.*, 11:90-100.
- Tomlinson, E. 1983. Enthalpy-entropy compensation analysis of pharmaceutical, biochemical, and biological systems. *Intern. J. of Pharmaceutics*, 13:115-144.
- U.S. EPA. 1990. Solvent extraction treatment. EPA/540/2-90/013, Engineering Bulletin, Office of Emergency and Remedial Response, U.S. EPA, Washington, DC.
- U.S. EPA. 1991. In situ soil flushing. EPA/540/2-91/021, Engineering Bulletin, Office of Emergency and Remedial. EPA, Washington, DC.
- Van de Venne, J.L.M. and J.L.H.M. Hendriks. 1978. Retention behaviour of carboxylic acids in reversed-phase column liquid chromatography. *J. Chromat.*, 167:1-16.

- van Uitert, LeGrand G. and Charles G. Haas. 1953. Studies on Coordination compounds. I. A method for determining thermodynamic equilibrium constants in mixed solvents. *J. of Am. Chem. Soc.*, 75:451-455.
- Verschueren, K. 1983. Handbook of Environmental Data of Organic Chemicals, 2nd ed. Van Nostrand Reinhold Company, New York, NY.
- Walters, G. 1982. Theoretical and experimental determination of matrix diffusion and related transport properties of fractured tuffs from the Nevada Test Site, LA-9471-MS. Los Alamos National Laboratory.
- Walters, R. and A. Guisepi-Ellie. 1988. Sorption of 2,3,7,8-tetrachlorodibenzo-p-dioxin to soils from water/methanol mixtures. *Envir. Sci. Tech.*, 22:819-825.
- Westall, J.C. 1984. Properties of organic compounds in relation to chemical binding. IN: Proceedings of a Symposium held in Stockholm, Nov. 17-19, 1983, pp. 65-90.
- Westall, J.C., C. Leuenberger, and R.P. Schwarzenbach. 1985. Influence of pH and ionic strength on aqueous-nonaqueous distribution of chlorinated phenols. *Environ. Sci. Tech.*, 19:193-198.
- Whitehurst, D., T.O. Mitchell, and Farcasiu. 1980. Coal liquefaction: The Chemistry and Technology of Thermal Processes., Academic Press, New York, NY.
- Wilson, G.M. and C.H. Deal. 1962. Activity coefficients and molecular structure. *Industrial Engineering and Chemistry Fundamentals*, 1:20-23.
- Wood, A.L., D.C. Bouchard, M.L. Brusseau, and P.S.C. Rao. 1990. Cosolvent effects on sorption and mobility of organic contaminants in soils. *Chemosphere*, 21: 575-587.
- Wood, A.L., D.C. Bouchard, and P.S.C. Rao. 1987. Sorption and transport of hydrophobic organic solutes in miscible solvent systems. Presented at the Annual Amer. Soc. Agron. Conf., Atlanta, GA, Nov. 20-Dec. 3. *Agron. Abstr.*, Amer. Soc. Agron., Madison, WI, p. 36.
- Woodburn, K.B., L.S. Lee, P.S.C. Rao, and J.J. Delfino. 1989. Comparison of sorption energetics for hydrophobic organic chemicals by synthetic and natural sorbents from methanol/water solvent mixtures. *Environ. Sci. Tech.*, 23:407-412.

- Woodburn, K.B., P.S.C. Rao, M. Fukui, and P. Nkedi-Kizza. 1986. Solvophobic approach for predicting sorption of hydrophobic organic chemicals on synthetic sorbents and soils. *Journal of Contaminant Hydrology*, 1:227-241.
- Yalkowsky, S.H. 1979. Estimation of entropies of fusion of organic compounds. *I&EC Fundam.*, 18:108-111.
- Yalkowsky, S.H. 1985. Solubility of organic solutes in mixed aqueous solvents. Project Completion Report, CR# 811852-01. U.S. Environmental Protection Agency, Ada, OK.
- Yalkowsky, S.H. 1987. Solubility of organic solutes in mixed aqueous solvents. Project Completion Report, CR# 812581-01. U.S. Environmental Protection Agency, Ada, OK.
- Yalkowsky, S.H., R.J. Orr, and S.C. Valvani. 1979. Solubility and partitioning. 3. The solubility of halobenzenes in water. *Ind. Chem. Eng. Fundam.*, 18:351.
- Yalkowsky, S.H. and T. Roseman. 1981. Solubilization of drugs by cosolvents. IN: *Techniques of Solubilization of Drugs*, S.H. Yalkowsky (Ed.). Marcel Dekker, Inc., New York, NY, pp. 91-134,
- Yalkowsky, S.H. and J.T. Rubino. 1984. Solubilization by cosolvents I: Organic solutes in propylene glycol-water mixtures. *Journal of Pharmaceutical Sciences*, 74:416-421.
- Yalkowsky, S.H. and S.C. Valvani. 1979. Solubilities and partitioning: 2. Relationships between aqueous solubilities, partition coefficients, and molecular surface areas of rigid aromatic hydrocarbons. *J. Chem. Eng. Data*, 24:127-129.
- Yalkowsky, S.H. and S.C. Valvani. 1980. Solubility and partitioning I: solubility of nonelectrolytes in water. *J. Pharm. Sci.*, 69:912-922.
- Zachara, J.M., C.C. Ainsworth, C.E. Cowan, B.L. Thomas. 1987. Sorption of binary mixtures of aromatic nitrogen heterocyclic compounds on subsurface materials. *Environmental Science and Technology*, 21:397-402.
- Zachara, J.M., C.C. Ainsworth, L.J. Felice, and C.T. Resch. 1986. Quinoline sorption to subsurface material: Role of pH and retention of the organic cation. *Env. Sci. Tech.*, 20:620-627.

- Zachara, J.M., C.C. Ainsworth, R.L. Schmidt, and C.T. Resch. 1988. Influence of cosolvents on quinoline sorption by subsurface materials and clays. *Journal of Contaminant Hydrology*, 1:343-364.
- Zachara, J.M., C.C. Ainsworth, and S.C. Smith. 1990. The sorption of N-heterocyclic compounds on reference and subsurface smectite clay isolates. *Journal of contaminant Hydrology*, 6:281-305.
- Zhong, W.Z., A.T. Lemley, and R. J. Wagenet. 1986. Quantifying Pesticide Adsorption and Degradation During Transport through Soil to Groundwater. American Chemistry Society Symposium Series No. 315. American Chemical Society, Washington, DC.

BIOGRAPHICAL SKETCH

Linda Shahrabani Lee was born in Dover, Delaware, in 1959. She graduated from Piper High School in Ft. Lauderdale, Florida, in 1977. Linda received a B.S. in chemistry from the University of Florida (Gainesville, Florida) in 1983 and her ACS certification in 1984.

During her undergraduate college career she worked as a technician in the Forest Soils laboratory in the Soil Science Department at UF. She also taught junior and senior high students for two years at the Westwood Hills Christian Academy. Linda was married in August of 1979 to Russell E. Lee. She has two sons, James Russell and Joshua Russell Lee, born in 1980 and 1989, respectively.

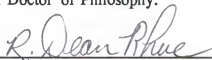
After receiving her B.S. degree, Linda worked as a chemist and lab manager in the Soil Physics laboratory in the Soil Science Department at UF where she received most of her laboratory training. She conducted studies in the fate and transport of toxic organic chemicals in aqueous and mixed solvent systems. Linda quickly became interested in the processes that affect chemical disposition in the environment which prompted her to pursue graduate study in both the environmental sciences and in soil science. Therefore, she pursued and completed a master's degree in environmental engineering sciences (May 1989) and during the following year initiated a Ph.D. program in the Soil & Water Science Department. Upon completion of her Ph.D. she will join the faculty at Purdue University in the Department of Agronomy with a 80/20 research/teaching appointment.

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P. Suresh C. Rao, Chair
Graduate Research Professor of
Soil and Water Science

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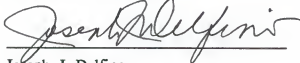
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Associate Professor of Soil and
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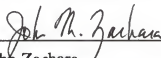
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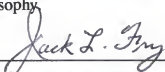
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This dissertation was submitted to the Graduate Faculty of the College of Agriculture and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 1993



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